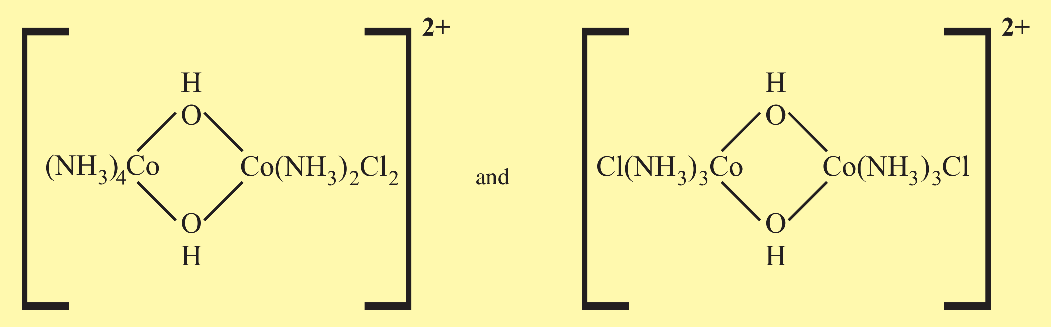
$[Co(NO_2)(NH_3)_5]^{2+}$ pentaamminenitrocobalt (III) ion and $[Co(O \cdot NO)(NH_3)_5]^{2+}$ pentaammine nitrito cobalt (III) ion and $[Co(NO_2)(NH_3)_5]Cl_2$ is yellow brown coloured and $[Co(O \cdot NO)(NH_3)_5]Cl_2$ is of red colour. Similarly CNS^- ion can be co-ordinated through nitrogen or sulphur and gives different isomers like. $[Mn(CO)_5SCN]^+$ and $[Mn(CO)_5NCS]^+$.

(ii) Co-ordination isomerism : When in co-ordination compounds, both positive ion and negative ion are complex ions then there is exchange between the two in the co-ordination sphere and isomers are formed e.g. $[Co(NH_3)_6]^{3+}$ $[Cr(CN)_6]^{3-}$ and $[Cr(NH_3)_6]^{3+}$ $[Co(CN)_6]^{3-}$; $[Cu(NH_3)_4]^{2+}$ $[PtCl_4]^{2-}$ and $[Pt(NH_3)_4]^{2+}$ $[CuCl_4]^{2-}$. This type of isomerism is observed when metal ion is in different oxidation states. e.g. $[Pt^{(II)}(NH_3)_4]$ $[Pt^{(IV)}Cl_6]$ and $[Pt^{(IV)}(NH_3)_4Cl_2]$ $[Pt^{(II)}Cl_4]$ **specific type of co-ordination isomerism is called position isomerism which is observed in cyclic complex compounds.**



(iii) Ionisation isomerism : The compounds whose propotion by weight and the component are same but they give different ions in solution, then that type of isomerism is called ionization isomerism. e.g.

$[Co(NH_3)_5NO_3]Cl$ and $[Co(NH_3)_5Cl]NO_3$

$[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$

$[Cr(NH_3)_4Cl_2]NO_2$ and $[Cr(NH_3)_4Cl \cdot NO_2]Cl$

(iv) Hydration isomerism : This type of isomerism is a special type of ionization isomerism. Three isomeric forms of $CrCl_3 \cdot 6H_2O$ are known.

(a) $[Cr(H_2O)_6]Cl_3$ (violet). If it is kept over H_2SO_4, it does not lose water and $3Cl^-$ and $3Ag^+$ ions take part in precipitation.

(b) $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ (gray green). If it is placed over H_2SO_4, then it loses one molecule of water and $2Cl^-$ ions take part in precipitation with $2Ag^+$ ions.

(c) If $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ (green) is placed over H_2SO_4 it loses 2 molecules of water and Cl^- ion takes part in precipitation with Ag^+ ion. Here, both ionization and hydration isomerisms are found. In such isomers, difference in their physical and chemical as well as colour is found.

Limitations of valence bond theory : When co-ordination compounds are formed, the valence bond theory is mostly applied for magnetic nature and structural formation. It has following limitations :

(i) It consists of some assumptions.

(ii) It cannot interpret quantitatively the magnetic information.

(iii) It is not able to explain the colours of co-ordination compounds.

(iv) It cannot interpret quantitatively thermodynamics and kinetic stabilities of co-ordination compounds.

(v) It does not make exact prediction regarding the tetrahedral and square planar structures of four co-ordination number complexes.

(vi) It cannot distinguish the weak and strong ligands.

4.11 Crystal Field Theory

Crystal Field Theory (CFT) is known as electrostatic model in which it is believed that there is ionic bond between metal and ligand. According to this theory, negatively charged ligand or polar neutral molecule forms ionic bond with metal ion. All the five types of d-orbitals are degenerate (same energy) in free gaseous form of metal atom or ion (Fig. 4.2). In addition to this, if there is spherical negatively charged field having spherical symmetry around the metal atom or ion, even then d-orbitals remain degenerate but when ligands are arranged around the metal atom or ion then the d-orbitals do not remain degenerate but gets split (fig. 4.3). The splitting of orbitals depends on the nature of crystal field.

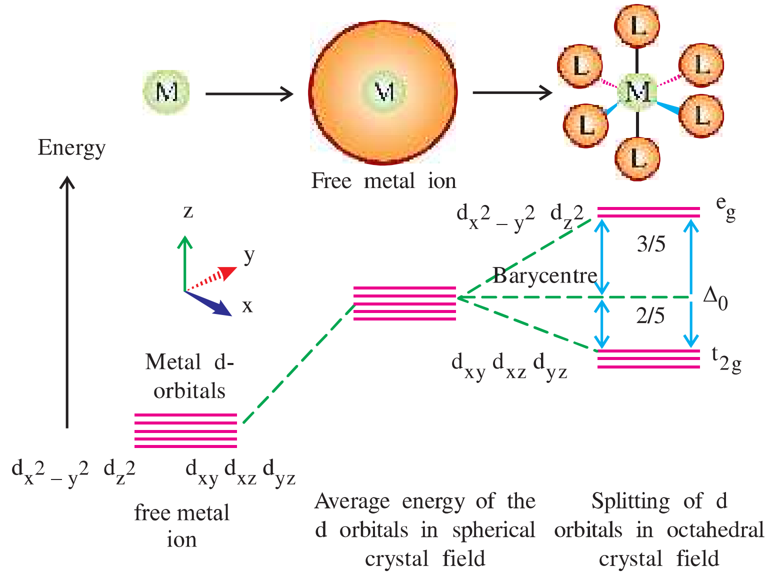


Fig. 4.3 d-orbital splitting in an octahedral crystal field

(A) Crystal field splitting in octahedral complexes : In octahedral complex, there are six ligands around the metal atom or ion. Here there is repulsion between electrons of d-orbital and electrons of ligand (or between negative ions); $d_{x^2-y^2}$ and d_{z^2} orbitals arranged on this axis experience more repulsion with ligand and will be raised in energy, while there is less repulsion between d_{xy}, d_{yz}, d_{xz} orbitals arranged between the axes, with ligand. Hence, their average energy of spherical crystal field decreases. As the degeneracy of these orbits is removed, it results into three orbitals having lower energy t_{2g} and higher energy possessing e_g orbitals. This type of phenomenon is called crystal field splitting. The splitting of energy of orbitals observed in octahedral complex is shown by Δ_0. Thus, in e_g orbitals there will be increase by $\frac{3}{5}\Delta_0$ and there will be $\frac{2}{5}\Delta_0$ decrese in energy of three t_{2g} orbitals.

The splitting of crystal field (Δ_0) depends on electric charge of metal ion and ligand. Some ligands produce strong field, so that the splitting of orbitals is more in proportion. While certain ligands produce weak field so that the splitting of orbitals is less in proportion. Generally, the series of ligands on the basis of increase in strength of fields by ligands, can be shown as below :

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA < NH_3 < en < NO_2^- < CN^- < CO$

The above series is called spectrochemical series. If in the metal ion, there are 1, 2 or 3 electrons in d-orbitals, then their arrangement will be in t_{2g} orbitals having low energy, according to Hund's rule. But if there are 4 electrons(d^4) in the d-orbitals then there are two possibilities as follows :

(i) The fourth electron will be arranged by pairing with any one electron present in t_{2g} orbitals.

(ii) The fourth electron will be arranged in e_g orbital neglecting giving energy for pairing.

Which of the above two possibilities can be possible depends on the splitting of crystal field (Δ_0) and on reactive magnitude energy of pairing; p.

(a) If $\Delta_0 < p$ then the fourth electron will be arranged in e_g orbital so that electronic structure will be $t_{2g}^{3}\ e_g^{1}$. For the ligands producing weak field, $\Delta_0 < p$ and form complexes having higher spins.

(b) If $\Delta_0 > p$ then the fourth electron will be arranged in t_{2g} orbital so that the electronic structure will be $t_{2g}^{4}\ e_g^{0}$ for ligands producing strong field $\Delta_0 > p$ and for complexes having low spins.

Experimental findings suggest that for complexes having d^4 to d^7 electronic configuration the ligands having stronger field give more stability than complexes having weak field.

(B) Crystal Field Splitting in Tetrahedral Complexes : In the formation of tetrahedral structure, the splitting of d-orbitals is in opposite nature to octahedral complexes. Like octahedral, if tetrahedral complex possesses equal distance between, metal, ligand, metal-ligand, then $\Delta_t = \frac{4}{9}\Delta_0$. Hence if the value of Δ_t is not sufficiently high, pairing of electrons does not occur. Hence low spin is observed in less proportions. The splitting of d-orbitals in tetrahedral structure is shown in the fig. 4.4.

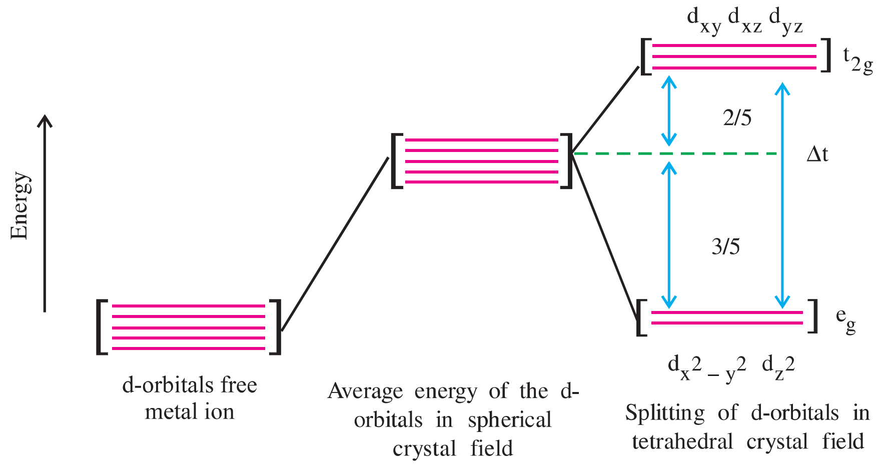


Fig. 4.4 d-orbital splitting in a tetrahedral crystal field

Colour in co-ordination compounds : We have studied earlier that the transition metal complexes exhibit wide variety of colours, which is one of their important properties. **This means that when white light passes through the sample, then it forms definite visible spectrum.** Others are removed from the white light. Hence, for a long time white light is not obtained. The absorption of colour is one complementary matter. The complementary colour is dependent on the wavelength If complex absorbs green colour, then it will be seen red.

In the table 4.5 absorption of different wavelengths and observed colours are shown.

Table 4.5 Absorbed wavelength of light and observed colour of complex compounds

Co-ordination compounds	Absorbed light wavelength nm	Absorbed colour of light	Colour observed of co-ordination compounds
$[CoCl(NH_3)_3]^{2+}$	535	Yellow 🟨	Violet 🟪
$[Co(NH_3)_3(H_2O)]^{3+}$	500	Bluish green 🟩	Red 🟥
$[Co(NH_3)_6]^{3+}$	475	Blue 🟦	Yellowish orange 🟧
$[Co(CN)_6]^{3+}$	310	Ultraviolet 🟪	Light yellow 🟨
$[Cu(H_2O)]^{2+}$	600	Red 🟥	Blue 🟦
$[Ti(H_2O)_6]^{3+}$	498	Bluish green 🟩	Light violet 🟪

The colours of co-ordination compounds can be explained on the basis of crystal field theory. e.g. $[Ti(H_2O)_6]^{3+}$, which has violet colour. This is octahedral complex in which one electron of d-orbital from metal ion complex is in stable state at t_{2g} one electron. (One electron Ti^{3+} is of $3d^1$ system) e_g state is vacant. If photon energy is by absorption of photon with yellow-green light, then the electron goes from t_{2g} layer to e_g layer ($t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$). Because of this, violet colour is shown. (As shown in fig. 4.5).

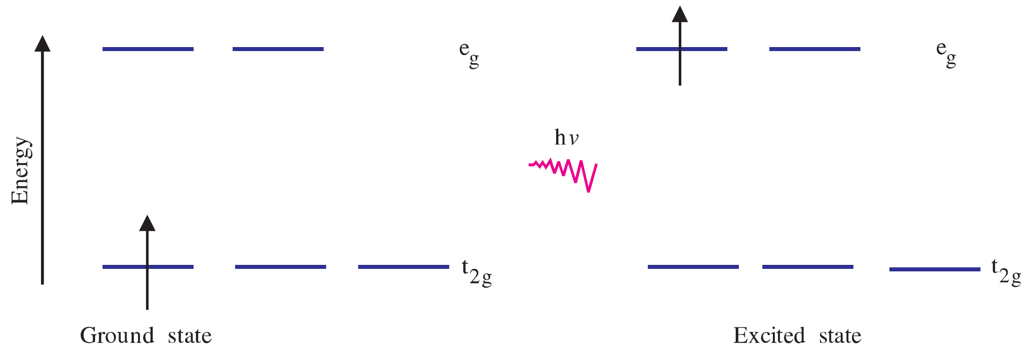


Fig. 4.5 Transition of an electron in $[Ti(H_2O)_6]^{3+}$

Here, one point is to be noted that in the absence of ligand, there is no splitting in crystal field. So the substance is colourless viz. $[Ti(H_2O)_6]Cl_3$; when heated water is removed and so it is changed to colourless substance. Similarly anhydrous $CuSO_4$ is white while $CuSO_4 \cdot 5H_2O$ is of blue colour.

The effect of ligand in complex can be explained by the example of $[Ni(H_2O)_6]^{2+}$. This complex is formed by dissolving $NiCl_2$ in water. Now, if didentate ligand ethane 1,2 diamine (en) is slowly added so that the molar ratio of en and Ni (en:Ni); is 1:1, 2:1, 3:1, the corresponding change in colour of complex is as follows :

$$[Ni(H_2O)_6]^{2+}(aq) + en(aq) = [Ni(H_2O)_4(en)]^{2+}(aq) + H_2O$$

green light blue

$$[Ni(H_2O)_4(en)]^{2+}(aq) + en(aq) = [Ni(H_2O)_2(en)_2]^{2+}(aq) + 2H_2O$$

blue / light violet

$$[Ni(H_2O)_2(en)_2]^{2+}(aq) + en(aq) = [Ni(en)_3]^{2+}(aq) + 2H_2O$$

violet

This series of colours is shown in fig. 4.6

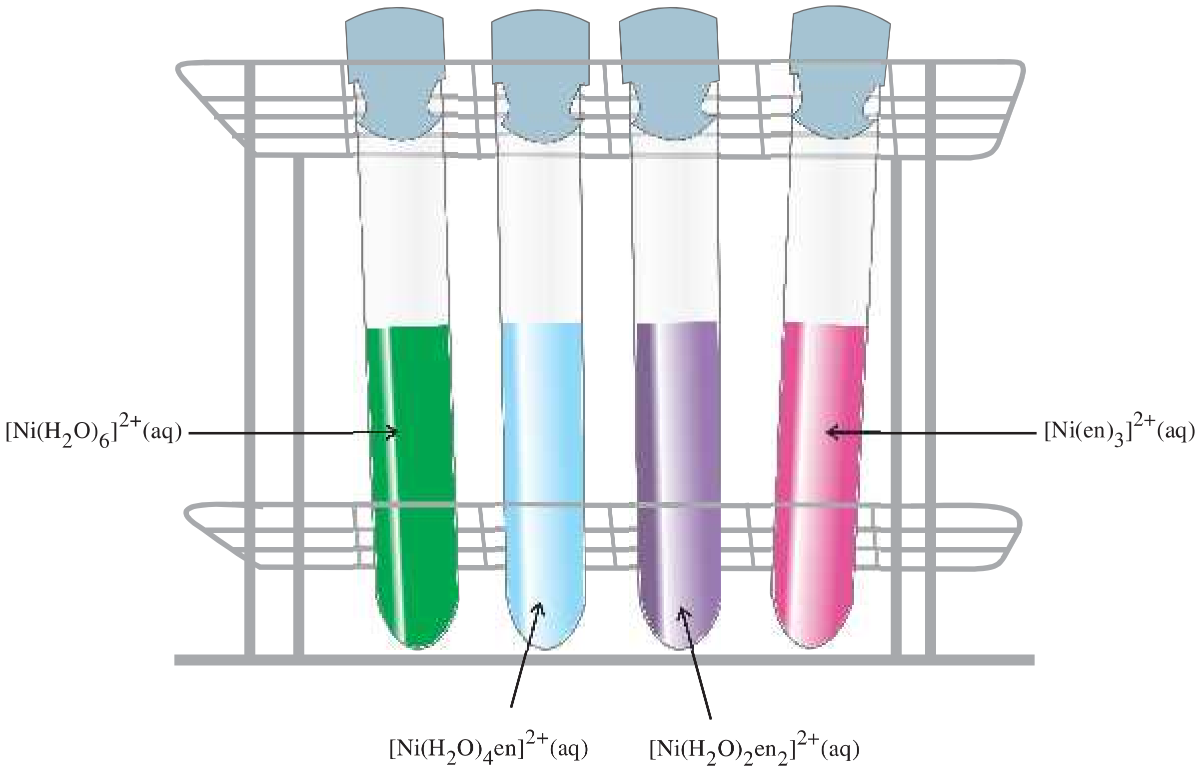


Fig. 4.6 Aqueous solutions of complex of nickel(II) with an increasing number of moles of ethane-1,2-diamine ligand

The magnetic properties, colour and the formation of structures of complex compounds can be successfully explained by crystal field model. The effect of many diversities is observed in charge of ligand and the ionic ligands. The position of anionic ligand is observed at the lower end in the spectrochemical series. Also there is no covalent bond character in bonding of central atom and that ligand. Thus, the limitation of CFT led to the development of field of study of molecular orbital theory.

The importance and uses (applications) of complex compounds : Co-ordination compounds. have wide range of applications and hence are very useful in mineral nutrition of plants and animals. It plays an important role in analytical chemistry. It possesses great utility in metallurgy, biological system and industries and drugs. They can be described as follows :

- Co-ordination compounds are useful in quantitative and qualitative methods in chemical analysis. We are familiar with the colour produced by their reaction on the basis of number of ligands with metal ions, (especially chelating ligands). Because of the results of the co-ordination compounds, the information about their proportion can be inferred and analysis can be carried out by classical and different instrumental methods. e.g. EDTA, DMG (Dimethyl glyoxime), α-nitroso-β-naphthol, cupferron, etc.

- By titration of hard water with Na_2EDTA the hardness of water can be determined. Ca^{2+} and Mg^{2+} ions give stable complexes with EDTA. The measurement of the order of stability of calcium and magnesium complexes with these ions can be carried out.

- In some important metal reactions such as silver or gold form important complexes. e.g. Gold is combined with cyanide in presence of oxygen and water, combine and solution of $[Au(CN)_2]^-$ is prepared from this solution. Gold can be obtained in metal form by addition of zinc.

- From co-ordination compounds, like successive decomposition reacts, the metals are formed by purification of metals. e.g. $[Ni(CO)_4]$ obtained from impure nickel. Then pure nickel is obtained from it by decomposition.

- Co-ordination compounds are very important in biological systems. The dye matter chlorophyll formed by magnesium is responsible for photosynthesis. Iron containing co-ordination compound haemoglobin dye-matter conducts O_2 and so red colour of blood is observed. Cobalt contains co-ordination conpound vitamin B_{12} or cyanocobalamine which is an-timatter of petnicious anemia. The other compounds which are substances having biological importance are in enzyme formed by formation of compound with metal viz. carboxypeptidase and carbonic anhydrade (catalysts of biological system-Enzymes).

- Co-ordination compounds are useful as catalysts in many industrial reactions e.g. Rhodium complex $[(Ph_3P)_3RhCl]$ which is useful as Wilkinson catalyst in dehydrogenation of alkanes.

- By electroplating with silver and gold soft, attractive replicas are prepared through handicraft. Replicas can be made from complexes $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ solutions also can be prepared from simple metal ion solutions.

- Film is stabilized by washing with solution of hypo (sodium thiosulphate) in white and black photography which is soluble in non-decomposable AgBr whose formation takes place from complex ion $[Ag(S_2O_3)_2]^{3-}$.

- In medicinal chemistry, chelate therapy is the important emerging method. For diagnosis of problem like presence of poisonous property of metals in plants and animals is a useful example. To remove the excess proportion of copper and iron, chelating ligands D-Penicilamine and desferrioxime are used for formation of co-ordinate compounds. EDTA is used for diagnostic test for poisoning of lead. From some co-ordinate compounds, the compound like platinum is useful in inhibiting the growth of tumours. e.g. cisplatin and related compound.

SUMMARY

- The salt that is obtained when two or more salts having independent existence combine according to the laws of combination and which maintain the properties of original salts is called double salt e.g. Alum is a double salt.
- Similarly, the compound that is obtained when two or more salts having independent existence combine according to laws of chemical combination and compound having new properties, formed is called complex compound. e.g. $K_3[Fe(CN)_6]$ is a complex salt.
- Most of the complex compounds are formed by elements of d-block (transition elements). In the electronic configuration of these elements, there is successive arrangement of electrons in d-orbitals. when the atom or ion of transition elements has vacant (n–1)d, ns and np or ns, np and nd orbitals, these transition elements accept negative ions or neutral molecules and they form the compounds which are called complex compounds. In this type of compounds, the bond that is formed between metal ions of elements and the negative ion or neutral molecules is called co-ordinate covalent bond. Around the centre of the metal ions of the molecules of these compounds, the negative ions or neutral molecules are combined with co-ordinate covalent bond.
- Alfred Werner, first of all gave the theory for complex compounds which is known as Werner's co-ordination theory. Some metals have the secondary valency in addition to their primary valence. By this the ions of that metal combine strongly with the negative ion or neutral molecules in first attraction sphere [ ].
- According to Werner's theory, the metal ion possesses two types of valencies : Primary valency and secondary valency.
- The primary valency of the metal is equal to its oxidation number or equal to the positive electric charge of the positive ion, which forms ionic bond, so that it gets ionized. The negative ion combines with primary valency.
- The secondary valency depends on the vacant orbitals in metal ion. The secondary valency is satisfied by negative ions or neutral molecules. It does not get ionized. The secondary valency mentions its co-ordination number. The secondary valency is fixed for the metal ion but now, it has been proved that the transition metal ions possess more than one co-ordination number. As the secondary valence being directional determines the geometrical shape of complex compound. From the magnetic properties also the shape of complex can be determined. e.g. In $[Cr(NH_3)_6]Cl_3$, Cr is metal ion and six molecules of neutral molecule ammonia (NH_3) are combined with it by secondary valency which do not get ionized. Hence, the co-ordination number is six. Three Cl^- are combined by primary valency which gets ionized. Hence the primary valency of Cr is three.
- Ligand is an ion having negative electric charge or neutral molecule. The classification of ligand is made on the basis of the number of electron pair donating atoms.

- If the negative ion or neutral molecule in the ligand forms one co-ordinate covalent bond by giving one electron pair to metal ion, then it is called unidentate ligand. Neutral molecules like H_2O, NH_3, CO, NO and negative ions like Cl^-, Br^-, CN^- act as unidentate ligands.

- The ligand which donates two electron pairs to metal ion, and form two co-ordinate covalent bonds is called didentate ligand. e.g. ethane 1,2-diamine (en), neutral and SO_4^{2-}, CO_3^{2-} negative ions act as didentate ligands.

- The ligand in which three co-ordinate sites are indicated then it is called tridentate. In this type of ligand the atoms donate three pairs of electrons to metal ion and form three co-ordinate covalent bonds. e.g. Propane-1, 2, 3-triamine (ptn) neutral and PO_4^{3-}, AsO_4^{3-} act as negative tridentate ligand.

- Six atoms in EDTA, (ethylene diaminetetracetate) ion, the six atoms donate six electron pairs and form six co-ordinate covalent bonds, which act as hexadentate ligand.

- Generally, the ligand in which two or more than two co-ordination sites are indicated, or the ligand in which two or more than two atoms form co-ordinate covalent bonds by donating electron pairs to metal ion is called polydenate ligand, which combines with metal ion and form complex compounds. They are called chelate compounds which are cyclic and possess higher stablity.

- The basic requirements for formation of complex compounds are ligand which can easily donate electron pairs, there must be vacant d-orbitals in the metal ion to accept electron pairs and the metal ion should have the symmetry same as that of the ligand.

  The ion satisfying these basic requirements can easily form complex compounds.

- The strength of formation of co-ordinate covalent bonds of different ligands being different, the stronger ligand possesses more attraction towards metal ion and form strong coordinate covalent bond. As a result, the stability of complex having strong ligand is more and the weak ligand containing complex compounds have less stability e.g. The strength of $[Ni(CN)_4]^{2-}$ is more than that of $[NiCl_4]^{2-}$.

- A complex compound, in which different types of ligands combine with metal ion and form complex compound, is called mixed ligand complex. If in any of the complex compounds only one metal ion is present, then it is called unicentred complex compound. If in any complex compound, more than one metal ions are present then it is called polycentred complex compound. In such unicentred or polycentred complex compounds, the three dimensional arrangement of ligand, the different geometrical structures are produced in co-ordination compounds, it is called polyhedra. Mostly the geometrical structures are of shapes-tetrahedral square planar, octahedral square pyramidal, trigonal bipyramidal. To understand these geometrical structures, the hybridization of orbitals of metal ion and magnetic properties are very useful. sp^3 hybridisation, dsp^2 hybridisation, d^3s hybridization in metal ions of co-ordination number four is seen. In sp^3d^2 hybridization and d^2sp^3 hybridization, the metal ions of transition elements is seen in metal ions having co-ordination number six. The metal ions of transition elements, magnetic moments of complex compounds of ions, their geometrical structures, types of ligands etc. are described.

- The nomenclature of complex compounds keeping in mind the rules of IUPAC is carried out. In complex compounds the rules are applicable.
- In nomenclature in co-ordination sphere, the name of the ligand according to English alphabets are first mentioned. Then the name of metal is written. The suffix "O" is attached after the name of negatively charged ligand. The name of the neutral ligand is mentioned as its original name. If the number of same ligand is more than the one the prefixes di, tri, tetra…etc. are applied. In the prefix of organic ligand, the prefix is a number then the ligand is placed in bracket and the prefix bis, tris, are attached. If the complex is negative ion then the name of ligand is written first and, in the end the suffix 'ate' is applied to the metal ion. Its oxidation state is shown in Roman number in bracket. If the complex is positive ion or neutral molecule, then successively writing the name of ligand, the name of metal is added at the end and oxidation state is shown in the Roman number.
- The geometry of complex compounds and magnetic properties of the complex depends on the hybridization in it. In complexes having co-ordination number 6 if strong ligand is attached with metal ion in complex, the oxidation state is shown in Roman numbers.
- In complex compounds, the geometrical structures are dependent on hybridization in it. In complex having co-ordination number 4, if the strong ligand is combined with metal ion then dsp^2 hybridization takes place in the complex and the structure is square planar. The example of this are $[Ni(CN)_4]^{2-}$, $[Ni(NH_3)_4]^{2+}$ etc. If the co-ordination number is 4 in the complex, and the weak ligand combines with the metal ion then sp^3 hybridization takes place e.g. $[NiF_4]^{2-}$, $[Ni(H_2O)_4]^{2+}$, etc. If the co-ordination number in complex ion is six, and the strong ligand is combined with metal ion, then d^2sp^3 hybridization and if weak ligand is combined with metal ion, then sp^3d^2 hybridization takes place, e.g. In $[Cr(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_6]^{3+}$ d^2sp^3 hybridization is there, while in $[FeF_6]^{4-}$, $[Fe(H_2O)_6]^{2+}$ sp^3d^2 hybridization is there. In MnO_4^- and CrO_4^{2-} there is d^3s hybridization, there are no unpaired electrons in d-orbital due to Mn^{7+} and Cr^{6+} oxidation states; but d-d transition takes place by electrons of ligand, and so it becomes coloured.
- Three types of isomerism are observed in complex compounds-geometrical isomerism, optical isomerism and structural isomerism.

- In geometrical isomerism, complex compounds having co-ordination number four- ML_2A_2 type, cis and trans isomerism is observed. In complex compounds having co-ordination number six - ML_4A_2 type, cis and trans while in ML_3A_3 facial and meridional isomerism are observed. In optical isomerism, leavo and dextro isomers are observed.

- In structural isomerism, ionic isomerism, hydration isomerism, co-ordination number isomerism and linkage isomerism are observed.

- In formation of co-ordination compounds the magnetic nature and structural formation with the help of valence bond theory; it has limitations. It cannot interpret the quantitatively the magnetic information and can not explain about the colour in co-ordination compounds. It can not give meaning of thermodynamical stability of co-ordination compounds, also it is not able to detect the difference between weak and strong ligand. To overcome these limitations the crystal field theory (CFT) was presented.

- Crystal field theory is known as electrostatic model in which it is believed that there is ionic bond between metal ion and ligand. According to this theory negatively charged ligand or neutral molecule forms ionic bond. In free metal atom in gaseous state, all the five types of d-orbitals are of equal energy (degenerate) but when ligands are arranged around the metal atom or ion in the complex, the d-orbitals do not remain of equal energy but get splitted. The splitting of orbitals depends on the nature of the crystal field.

- The crystal field splitting (Δ_0) depends on the field produced by electric charge of metal ion and the ligand. Some ligands produce strong field and so splitting is in more proportion. Some ligands produce weak field, so that the splitting is in less proportion. The series of ligands on the basis of the strength of the field produced by ligand can be shown as below :

  $I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3$ $< en < NO_2^- < CN^- < CO$: Spectrochemical series.

- Metal complexes have large magnitude of colours. When the white light passes through the sample, then it forms a specific visible spectrum and the remaining colours of white light are removed. The absorption of colour by complex compounds is dependent on wavelength. If green colour is absorbed then it appears of red colour.

- The colour of co-ordination compounds can be explained on the basis of crystal field theory e.g. $[Ti(H_2O)_6]^{3+}$ violet colour, $[Ni(H_2O)_6]^{2+}$ green colour, and $[Ni(en)_3]^{2+}$ violet colour,

- Co-ordination compounds have great importance. They have immense utility value in nutrition of minerals in plants and animals, analytical chemistry, metallurgy, biological systems and industries. They are also used in various drugs.

EXERCISE

1. Select the proper choice from the given multiple choices :

(1) What type of bond is L → M in complex compounds ?

(A) Ionic (B) Metallic

(C) Co-ordinate covalent (D) Covalent

(2) Who gave metal co-ordination theory ?

(A) Albert Werner (B) Schrodinger

(C) August Hofmann (D) Alfred Werner.

(3) What is the nature of ligand in complex compounds ?

(A) Bronsted-Lowry base (B) Lewis base

(C) Lewis acid (D) Arrhenius acid.

(4) Which of the following cannot act as ligand ?

(A) H_2O (B) NO_3^- (C) CO_2 (D) CO

(5) Which of the following compounds is a double salt ?

(A) Potassium permanganate (B) Ferrous ammonium sulphate

(C) Ammonium chromate (D) All the given.

(6) What is the primary valency of metal ion in the complex $[Co(en)_2Cl_2]NO_3$?

(A) 4 (B) 6 (C) 2 (D) 3

(7) What is the electrical charge of pentacarbonyl iron (0) complex ?

(A) one (B) two (C) three (D) zero

(8) What is the secondary valency of metal ion in $[Cr(NH_3)_4OX]NO_3$?

(A) 2 (B) 4 (C) 6 (D) 8

(9) What is the valency of Fe which does not ionize in $K_3[Fe(OX)_3]$?

(A) Three (B) Four (C) Six (D) One

(10) How many ions are obtained by ionization of $(NH_4)_2[MoO_4]$ complex compound in aqueous solution ?

(A) 2 (B) 4 (C) 0 (D) 3

(11) How many ions will be obtained by ionization of ferric hexacyanoferrate(III) complex compound ?

(A) 7 (B) 4 (C) 2 (D) 3

(12) What is the geometrical shape of $K_4[Ni(CN)_4]$?

(A) Octahedral (B) Square planar

(C) Tetrahedral (D) Trigonal pyramidal

(13) Which of the following is not the chelating ligand ?

(A) en (B) ptn (C) OX^{2-} (D) CO

(14) O^{2-} is the example of what type of ligand ?

(A) Didentate (B) Tridentate (C) Unidentate (D) Hexadentate.

(15) How many co-ordination sites are in edta ligand ?

(A) six (B) four (C) three (D) two

(16) What will be the hybridization in $[Ni(CN)_4]^{2-}$ complex ion ?

(A) sp^3 (B) dsp^2 (C) sp^3d^2 (D) d^2sp^3

(17) Which of the following compounds possesses paramagnetic property ?

(A) $[Ni(NH_3)_4]^{2+}$ (B) $[Fe(CN)_6]^{4-}$ (C) $[Co(NH_3)_6]^{3+}$ (D) $[Fe(CN)_6]^{3-}$

(18) By which of the following, poisoning of lead in the body can be removed ?

(A) ptn (B) EDTA (C) pn (D) OX^{2-}

(19) Which complex is used to stop the growth of tumour in body ?

(A) Chlorophyll (B) Cisplatin (C) Haemoglobin (D) Ferrocene.

(20) What is the colour of $[Ni(H_2O)_6]^{2+}$ complex compound ?

(A) Violet (B) Green (C) Blue (D) Pink

(21) Mention the electric charge on edta.

(A) 6- (B) 2- (C) 3- (D) 4-

(22) Which of the following complex ion does not possess tetrahedral shape ?

(A) $[MnO_4]^-$ (B) $[Ni(CO)_4]$ (C) $[Ni(CN)_4]^{2-}$ (D) $[Cu(NH_3)_4]^{2+}$

(23) What is theoretical magnetic moment of complex compound $K_2[NiF_4]$?

(A) 1.73 BM (B) 2.83 BM (C) 3.87 BM (D) Zero.

(24) Which of the following ligands acts as strongest ligand ?

(A) Cl^- (B) NH_3 (C) CO (D) CN^-

(25) The number of Cl^- combined by secondary valency in $[Fe(NH_3)_4Cl_2]Cl$ is ....

(A) 1 (B) 2 (C) 3 (D) 0

(26) Which of the following complex ions is most stable ?

(A) $[FeCl_6]^{3-}$ (B) $[Fe(H_2O)_6]^{3+}$ (C) $[Fe(NH_3)_6]^{3+}$ (D) $[Fe(CN)_6]^{4-}$

(27) Which of the following complex ions does not possess optical isomerism ?

(A) $[Co(en)(NH_3)_4]^{2+}$ (B) $[Co(H_2O)_4(en)]^{3+}$

(C) $[Co(en)_2(NH_3)_2]^{2+}$ (D) $[Co(NH_3)_3CI_3]^{+}$

(28) Aqueous solution of which complex will be possessing high conductance ?

(A) Hexamminecobalt(III)chloride

(B) Tetramminedichloridocobalt(III)chloride

(C) Pentamminechloridocobalt(III)chloride

(D) Triamminetrichloridocobalt(III)

(29) Which of the following is the correct order of spectrochemical series ?

(A) $Cl^- < F^- < C_2O_4^{2-} < NO_2^- < CN^-$ (B) $F^- < Cl^- < NO_2^- < CN^- < C_2O_4^{2-}$

(C) $CN^- < C_2O_4^{2-} < Cl^- < NO_2^- < F^-$ (D) $C_2O_4^{2-} < F^- < Cl^- < NO_2^- < CN^-$

(30) Which transition of electrons will be observed in the following when Ti^{3+} ion having complex absorbs visible light ?

(A) $t_{2g}^0 e_g^1 \rightarrow t_{2g}^1 e_g^0$ (B) $t_{2g}^2 e_g^0 \rightarrow t_{2g}^1 e_g^1$ (C) $t_{2g}^1 e_g^1 \rightarrow t_{2g}^0 e_g^2$ (D) $t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$

(31) The co-ordination number, oxidation number, number of electrons in d-orbital and number of unpaired electrons is respectively in complex $[Co(NH_3)_4CO_3]ClO_4$

(A) 6, 3, 6, 0 (B) 7, 2, 7, 1 (C) 5, 2, 6, 4 (D) 6, 2, 7, 3

2. Answer the following questions in brief :

(1) What is meant by double salt ?

(2) What is meant by complex salt ?

(3) How many types of valencies, the metal ion possesses in complex compound ? and which ?

(4) Write the valencies of metal ion in $[Fe(CN)_6]^{4-}$ complex compound.

(5) What type of ligands are PO_4^{3-} and O^{2-} ?

(6) What type of bonds are present of the metal ion in complex compound ?

(7) What is meant by co-ordination site ?

(8) What is called ligand ?

(9) Why are the geometrical shapes produced in complexes ?

(10) What is meant by co-ordination covalent bond ?

(11) What is meant by secondary valency ? By which type of ions is it satisfied ?

(12) What is meant by polydentate ligand ? Give any one example.

(13) What is meant by chelate complex ? Give any one example.

(14) Draw the structure of $[M\text{-}EDTA]^{\pm n}$

(15) What is meant by mixed ligand complex ? Give an example.

(16) What is meant by unicentred and polycentred complex compounds ? Give an example.

(17) Give two examples of complex ions having co-ordination number 4 for different magnetic moments.

(18) Explain chelate therapy.

(19) In refining of which metal, the use of complex compounds is made ?

(20) Describe the use of edta.

(21) Mention limitations of crystal field theory.

(22) What type of isomerism is observed in $[Cr(NH_3)_4Cl_2]NO_2$?

(23) Mention how many types of isomerism are there in $[Pt(en)_2Cl_2]^{2+}$ complex ion and mention them.

(24) Give two examples of complex ions having sp^3d^2 hybridisation.

(25) Describe Werner's co-ordination theory.

3. Answer the following questions :

(1) Explain the difference between double salt and complex salt.

(2) What is called tridentate ligand ? Explain giving example.

(3) Explain giving example, hexadentate ligand.

(4) Mention the basic requirements for the formation of complex compounds.

(5) Explain stability of complex compounds.

(6) Explain sp^3d^2 and dsp^2 hybridisation.

(7) Explain the hybridization and geometrical structure of MnO_4^- complex ion.

(8) Explain geometrical isomerism.

(9) Explain optical isomerism.

(10) Write limitations of valence bond theory.

(11) Explain crystal field theory.

(12) Explain the application of complexes in biological systems and photography.

4. Answer the following questions in detail :

(1) Write the points of Werner's co-ordination theory.

(2) What is meant by ligand ? Explain its classification.

(3) Explain the hybridization of orbitals of metal ions in complex compounds and the magnetic properties.

(4) Explain the geometrical structures and magnetic properties of the following complex compounds with the help of hybridization. $[Ni(CN)_4]^{2-}$, $[Fe(CN)_6]^{3-}$, $[FeF_6]^{4-}$, $[Co(NH_3)_6]^{3+}$, $[NiCl_4]^{2-}$

(5) Explain in detail the structural isomerism with examples.

(6) Explain crystal field splitting in octahedral complexes and write the limitations of crystal field theory.

(7) Explain in detail, "Colour in co-ordination compounds."

(8) Describe the importance and applications of co-ordination compounds.

(9) Write the IUPAC names of the complex compounds shown below :

$K_3[Fe(CN)_5NO]$

$K_3[Fe(CN)_4Cl_2]$

$Na_3[Fe(OX)_3]$

$K_2[CoF_4]$

$(NH_4)[Co(CO_3)Cl_2]$

$Na[Cr(en)(OX)_2]$

$K_3[Co(CN)_6]$

$Na_2[CoCl_6]$

$Na_2[PtCl_6]$

$[Cr(NH_3)_6][Cr(NO_2)_6]$

$K_4[Cr(CN)_5NO]$

$[Pt(en)_2(CO)_2]Cl_4$

$[Au(CN)_4C_2O_4]^{3-}$

$(NH_4)_2[MoO_4]$

$NH_4[Co(H_2O)_2(NO_3)_4]$

$[Fe(H_2O)_6]Cl_2$

$[Cr(en)_2(pn)_2]Cl_3$

$[Co(H_2O)_4Cl_2]_2SO_4$

$Fe_3[Fe(CN)_6]_2$

$K_2[Fe(CN)_4(H_2O)CNO]$

$[Pt^{II}(NH_3)_4][Pt(OX)_3]$

$[Ni(NH_3)_2Cl_2]$

$[Cr(NH_3)_4CO_3]_3PO_4$

$[Ag(NH_3)_2][AgOX]$

$[MnO_4]^-$

●

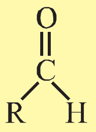
Unit

5

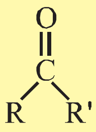
Aldehydes, Ketones and Carboxylic Acids

5.1 Introduction

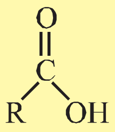
Organic compounds containing double bond ($>C=O$) between carbon and oxygen are called carbonyl compounds. In **aldehydes** the carbonyl group is attached to one hydrogen atom and one alkyl or aryl group, while in **ketones** it is attached to one alkyl and one aryl group or to two alkyl or two aryl groups, which may be same or different. If carbonyl group is attached to one hydroxyl group, the compounds are known as **carboxylic acids.** In carboxylic acid compounds, if the hydrogen of hydroxyl group is substituted by alkyl or aryl group, the compounds are known as **esters,** but if it is substituted by acyl group, the compounds are known as **acid anhydrides.** If the carbonyl group is attached to chloro and to amino group, the compounds are known as **acid chlorides** and **amides** respectively. The general formula of these compounds are as below :



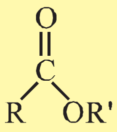
Aldehyde



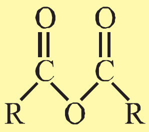
Ketone



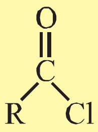
Carboxylic acid



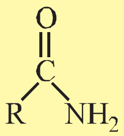
Ester



Anhydride



Acid chloride



Amide

Aldehydes and ketones have same general molecular formula $C_nH_{2n}O$, but have different functional groups, therefore, they **are called functional group isomers.** For example compounds having molecular formula C_3H_6O will be CH_3CH_2CHO which is aldehyde (functional group is aldehyde) and CH_3COCH_3 which is ketone (functional group is ketone).

5.2 Structure and Nomenclature of Carbonyl Group

Structure of Carbonyl Group : The $>C=O$ bond of carbonyl group in aldehyde and ketone is made up of one σ-bond and one π-bond. In the formation of carbonyl group compounds, the carbonyl carbon atom is sp^2 hybridised and forms three sp^2 hybrid orbitals. One of the sp^2 hybridised orbitals of carbon overlaps with p-orbital of oxygen atom forming a σ-bond between carbon and oxygen atom. The remaining two hybridised sp^2 orbitals of carbon atom, form additional two σ-bonds, either by overlapping with 1s-orbital of two hydrogen atoms as in formaldehyde or with 1s-orbital of one hydrogen atom and one sp^3 hybrid orbital of an alkyl group carbon in aldehydes other than formaldehyde or with two sp^3 hybrid orbitals of two alkyl groups carbon in ketones. All the three σ-bonds lie in the same plane and are inclined to one another at an angle 120^0 as shown in figure 5.1. The half-filled $2p_z$-orbital of carbon atom overlaps sideway with $2p_z$-orbital of oxygen atom to form a π-bond, and the electron cloud of the π-bond lies both above and below the C–O σ-bond. Thus, the carbonyl carbon and oxygen atoms and two atoms which are directly bonded to the carbonyl carbon lie in the plane as shown in figure. 5.1. This has been also confirmed by **electron diffraction** and **spectroscopic studies.**

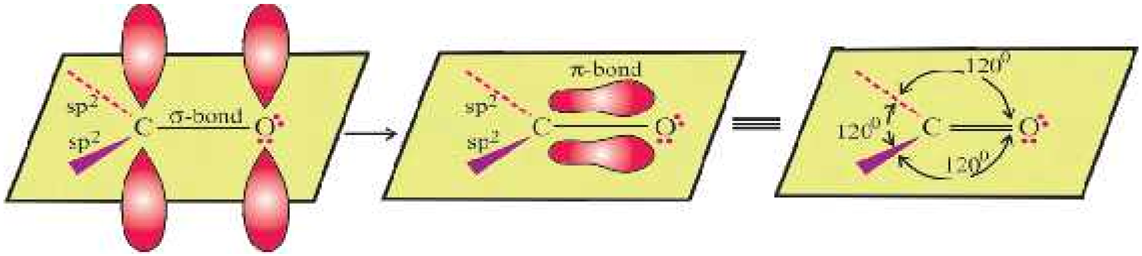


Fig 5.1 Orbital diagram for the formation of carbonyl group

Nature of carbonyl group : In carbonyl group the carbon-oxygen double bond is polarized due to higher electronegativity of oxygen atom relative to that of carbon atom. As a result the oxygen atom tends to attract the electron cloud of the π-bond towards itself as shown in figure 5.2. As a result the carbonyl carbon becomes an electrophile (Lewis acid) and oxygen becomes a nucleophile (Lewis base).

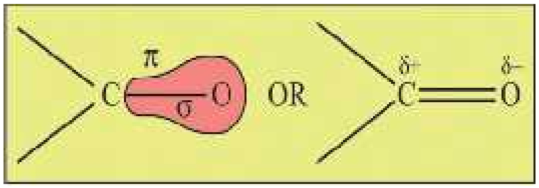
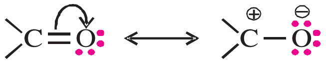


Fig 5.2 Electron cloud gets attracted more towards oxygen atom

Thus the carbonyl group is **polar in nature.** Hence, such compounds have dipole moments. For example, aldehydes and ketones have 2.3-2.8 D dipole moments. The high polarity of the carbonyl group is explained on the basis of resonance structures shown below :

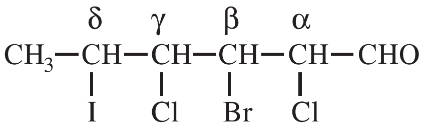


$$>C=\ddot{O}: \longleftrightarrow >\overset{\oplus}{C}-\overset{\ominus}{\ddot{O}}:$$

Nomenclature of carbonyl compounds :

Aldehydes and ketones-IUPAC and Common names : The common names of aldehydes are obtained by replacing the terminal **"-ic acid"** by **"aldehyde"** from the common name of the corresponding carboxylic acid. For example, formic acid, acetic acid, benzoic acid; their corresponding aldehydes are formaldehyde, acetaldehyde and benzaldehyde respectively. In substituted aldehydes the positions of the substituents are indicated by Greek alphabets α, β, γ, δ etc. with the carbon atom next to the –CHO group being designated as α.

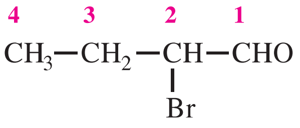
For example,



$$\mathrm{CH_3}-\underset{\mathrm{I}}{\overset{\delta}{\mathrm{CH}}}-\underset{\mathrm{Cl}}{\overset{\gamma}{\mathrm{CH}}}-\underset{\mathrm{Br}}{\overset{\beta}{\mathrm{CH}}}-\underset{\mathrm{Cl}}{\overset{\alpha}{\mathrm{CH}}}-\mathrm{CHO}$$

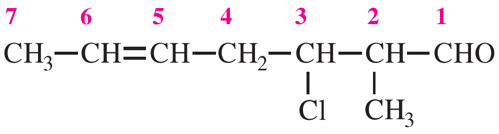
β-Bromo, α-γ dichloro, δ-iodo caproaldehyde

The IUPAC names of open chain aliphatic aldehydes are derived from the names of the corresponding hydrocarbon by replacing the terminal alphabet **'e' from its name by - 'al'.** e.g., methane, a hydrocarbon-its corresponding aldehyde, HCHO and its IUPAC name is methanal. In substituted aldehydes the carbon chain containing aldehyde group, the position of the subsituents are indicated by numbers. The numbering of the substituted aldehyde carbon chain is done in such a way so that the aldehyde group at end of the chain gets number 1. For example,



$$\overset{4}{\mathrm{CH_3}}-\overset{3}{\mathrm{CH_2}}-\underset{\mathrm{Br}}{\overset{2}{\mathrm{CH}}}-\overset{1}{\mathrm{CHO}}$$

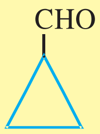
2-Bromobutanal



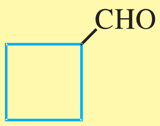
$$\overset{7}{\mathrm{CH_3}}-\overset{6}{\mathrm{CH}}=\overset{5}{\mathrm{CH}}-\overset{4}{\mathrm{CH_2}}-\underset{\mathrm{Cl}}{\overset{3}{\mathrm{CH}}}-\underset{\mathrm{CH_3}}{\overset{2}{\mathrm{CH}}}-\overset{1}{\mathrm{CHO}}$$

3-Chloro-2-methylhept-5-enal

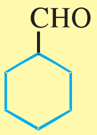
The IUPAC names of aliphatic cyclic aldehydes are given by adding **suffix carbaldehyde** after the full name of the cycloalkane. For example,



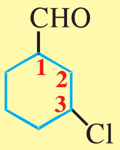
Cyclopropane
carbaldehyde



Cyclobutane
carbaldehyde

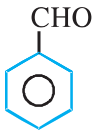


Cyclohexane
carbaldehyde

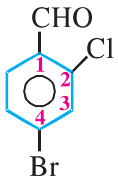


3-Chlorocyclo
hexanecarbaldehyde

The IUPAC names of aromatic aldehyde compounds - like aldehyde group on benzene ring are given by benzenecarbaldehyde (or benzaldehyde) and the position of the substituents are indicated by numbering, starting from the carbon having –CHO group. For example,



Benzenecarbaldehyde OR
benzaldehyde



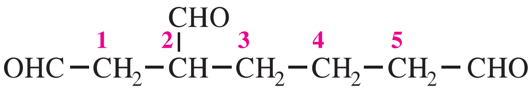
4-Bromo-2-chlorobenzene carbaldehyde
OR 4-bromo-2-chlorobenzaldehyde

When two aldehyde groups are linked to carbon chain then only such aliphatic compounds are named which includes the functional group in calculation of carbon numbers and suffix 'dial' is added. For example,

$\mathrm{OCH{-}CH_2{-}CH_2{-}CHO}$ Butanedial

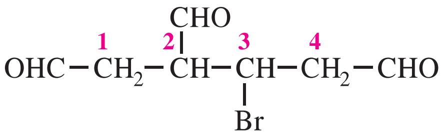
$\mathrm{OCH{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CHO}$ Haxanedial

When more than two aldehyde groups are linked to carbon chain then such compounds are named as a derivative of the hydrocarbon which does **not include the carbon atoms of the functional groups.** For example,



$$\mathrm{OHC}-\overset{1}{\mathrm{CH_2}}-\overset{\overset{\mathrm{CHO}}{|}}{\overset{2}{\mathrm{CH}}}-\overset{3}{\mathrm{CH_2}}-\overset{4}{\mathrm{CH_2}}-\overset{5}{\mathrm{CH_2}}-\mathrm{CHO}$$

Pentane-1,2,5-tricarbaldehyde

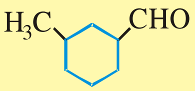
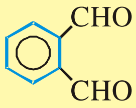
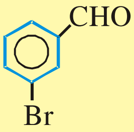


$$\mathrm{OHC}-\overset{1}{\mathrm{CH_2}}-\overset{\overset{\mathrm{CHO}}{|}}{\overset{2}{\mathrm{CH}}}-\underset{\underset{\mathrm{Br}}{|}}{\overset{3}{\mathrm{CH}}}-\overset{4}{\mathrm{CH_2}}-\mathrm{CHO}$$

3-Bromobutane-1,2,4-tricarbaldehyde

The common and IUPAC names of the aldehydes are given in table 5.1

Table 5.1 Common and IUPAC names of some aldehydes

Structure	Common name	IUPAC name
HCHO	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
$(CH_3)_2CHCHO$	Isobutyraldehyde	2-Methylpropanal
	γ-Methylcyclohexanal	3-Methylcyclohexanecarbaldehyde
$CH_3CH(OCH_3)CHO$	α-Methoxypropionaldehyde	2-Methoxypropanal
$CH_3CH_2CH_2CH_2CHO$	Valeraldehyde	Pentanal
$CH_2{=}CHCHO$	Acrolein	Prop-2-enal
	Phthaldehyde	Benzene-1,2-dicarbaldehyde
	m-Bromobenzaldehyde	3-Bromobenzenecarbaldehyde or 3-Bromobenzaldehyde

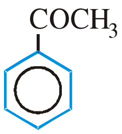
The common names of the aliphatic and aromatic ketones are obtained by naming the two alkyl or aryl groups (in the alphabetical order) attached to the ketone group as two separate words and adding the suffix ketone. If both the attaching groups are same the **prefix di is used.** For example,

CH_3COCH_3

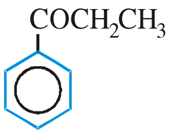
Dimethylketone

$CH_3COCH_2CH_3$

Ethylmethylketone



Methylphenylketone



Ethylphenylketone

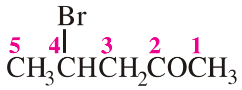
The IUPAC names of ketones are derived from the name of corresponding hydrocarbon by replacing the terminal alphabet **'e' by the suffix 'one'.** For substituted ketones the positions of the substituents are indicated by numbering the chain in such a way that the keto group gets the lowest number. For example,

CH_3COCH_3

Propan-2-one

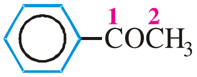
OR

Propanone

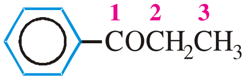


$$\overset{5}{CH_3}\overset{4}{C}\overset{Br}{H}\overset{3}{C}H_2\overset{2}{C}O\overset{1}{C}H_3$$

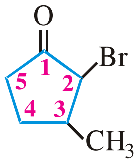
4-Bromopentan-2-one



1-Phenylethan-1-one



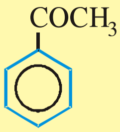
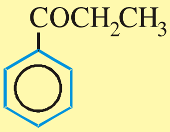
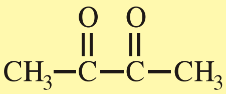
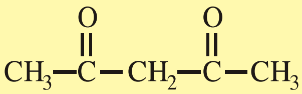
1-Phenylpropan-1-one



2-Bromo-3-methylcyclopentanone

The common and IUPAC names of the ketones are given in table 5.2

Table 5.2 Common and IUPAC names of some ketones

Structure	Common name	IUPAC name
$CH_3COCH_2CH_2CH_3$	Methyl n-propyl ketone	Pentan-2-one
$(CH_3)_2CHCOCH(CH_3)_2$	Diisopropyl ketone	2,4-Dimethylpentan-3-one
	α-Methylcyclohexanone	2-Methylcyclohexanone
$(CH_3)_2C=CHCOCH_3$	Mesityl oxide	4-Methylpent-3-en-2-one
	Methylphenylketone OR Acetophenone	1-Phenylethan-1-one
	Ethyl phenyl ketone	1-Phenylpropan-1-one
 $CH_3-\overset{O}{\overset{\Vert}{C}}-\overset{O}{\overset{\Vert}{C}}-CH_3$	Biacetyl	Butane-2,3-dione
 $CH_3-\overset{O}{\overset{\Vert}{C}}-CH_2-\overset{O}{\overset{\Vert}{C}}-CH_3$	Acetyl acetone	Pentane-2,4-dione

5.3 Physical Properties of Aldehydes and Ketones

Aldehydes and ketones possess polar carbonyl group and hence exhibit weak intermolecular association due to **dipole-dipole** interactions between the opposite ends of the $>C=O$ dipoles.

Intermolecular dipole-dipole attraction

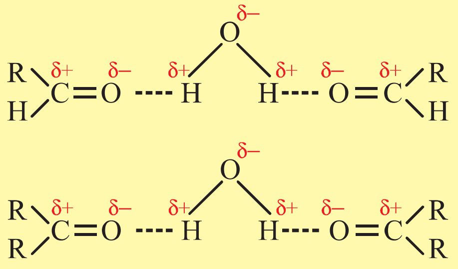
So, the boiling points of aldehydes and ketones are a little higher than non-polar compounds like hydrocarbons and weakly polar compounds like ethers of comparable molecular mass. The boiling points of aldehydes and ketones are lower than those of alcohols and carboxylic acids of comparable molecular mass because in carboxylic acid and alcohol molecules there exists an intermolecular hydrogen bonding which is stronger than dipole-dipole interaction. Among the isomeric aldehydes and ketones, the ketones have slightly higher boiling points. This happens due to the presence of two electron-donating alkyl groups around the carbonyl group which makes them more polar, so the order of boiling points is **carboxylic acid > alcohol > isomeric ketone > isomeric aldehyde > ether > hydrocarbon.**

The boiling points of comparable molecular mass of the following compounds are given in table 5.3.

Table 5.3 Boiling points of some organic compounds

Compound	Boiling point (K)	Molecular mass
n-Butane	273	58
Methoxyethane	281	60
Propanal	322	58
Propanone	329	58
Propan-1-ol	370	60
Ethanoic acid	391	60

The lower members of aldehydes and ketones upto three carbon atoms such as methanal, ethanal, propanal and propanone are soluble in water due to hydrogen bond formation between the polar carbonyl group and the water molecules.



Hydrogen bonding of aldehyde and ketone with water molecules

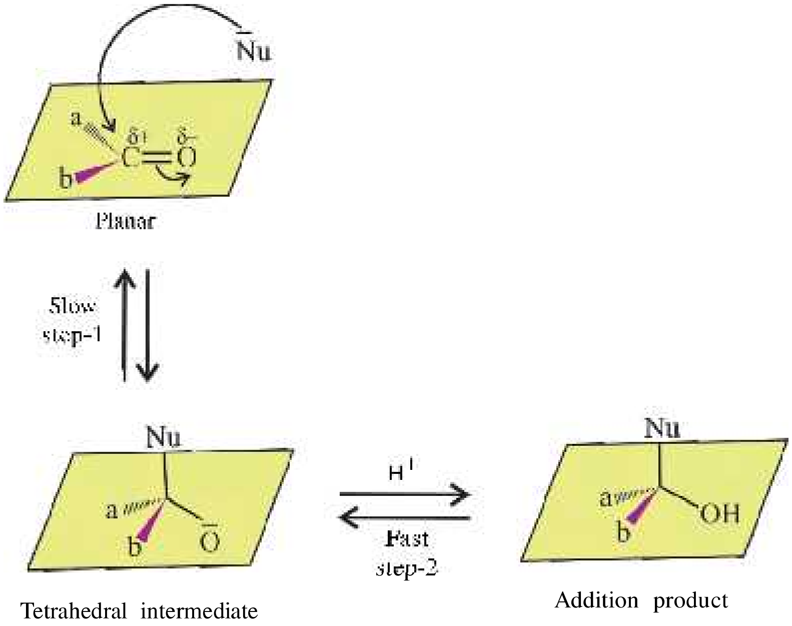
But the solubility of aldehydes and ketones in water decreases rapidly with the increase in length of alkyl chains. Similarly the solubility of aromatic aldehydes and ketones is much lower than their corresponding aliphatic aldehydes and ketones due to the presence of larger hydrocarbon parts (like benzene ring etc.). However all aldehydes and ketones are fairly soluble in organic solvents like benzene, ether, alcohol, chloroform etc. The lower aldehydes have strong pungent odours, but as the size of the aldehyde molecules increases the odour becomes less pungent and more fragrant. However, the ketones are generally in liquid forms having pleasant smell. A number of naturally occurring aldehydes and ketones are used in the preparation and blending of perfumes and as flavouring agents.

5.4 Chemical Reactions of Aldehydes and Ketones

Aldehydes and ketones have the same functional group i.e. polarized carbonyl group. So they undergo similar chemical reactions. However, the presence of a hydrogen atom on the carbonyl group of aldehydes makes them much **more reactive than ketones.** This hydrogen atom is responsible for many reactions of aldehydes and thus they differ from ketones. Some chemical reactions of aldehydes and ketones are as follows :

(i) Nucleophilic addition reactions : Aldehydes and ketones have the carbonyl group containing double bond and so they can undergo addition reactions. Alkenes have $\rangle C=C\langle$ and they undergo electrophilic addition reactions, while the aldehydes and ketones undergo nucleophilic addition reactions because the **carbonyl group is polar and the carbon atom is slightly positively charged which is readily attracted by the nucleophile.**

The mechanism of nucleophilic addition reactions : The structure of carbonyl group is planar and it is polar, so the nucleophile is attracted to the positively charged carbon atom of carbonyl group either from above or below the plane of sp^2 hybridised orbital of carbonyl group. So it results in formation of an anion (tetrahedral alkoxide) by the complete transfer of π-electrons of the carbon-oxygen double bond to the oxygen atom. During this process, the hybridisation of carbon atom changes from sp^2 to sp^3 and hence, the oxygen atom gets pushed out of the plane of the carbonyl group and **form new carbon nucleophile (Nu) bond which is slow step so, it is the rate determining step and it is also reversible.** In the second step the proton (which is obtained from weak acidic medium) gets attracted by oxygen of carbonyl group (tetrahedral alkoxide) and the electrically neutral product is formed. **The second step is also reversible.**



Relative reactivities of aldehydes and ketones : Aldehydes are generally more reactive than corresponding ketones in nucleophilic addition reaction, due to the following reasons.

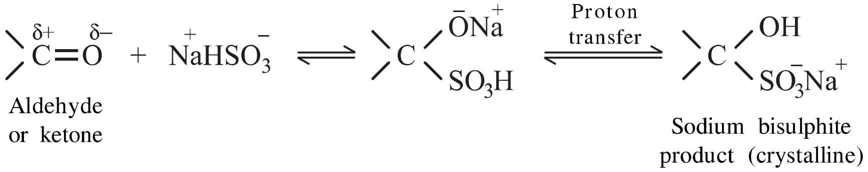
(i) Steric effects : As the number and size of the alkyl group attached to the carbonyl group increases, the attachment of nucleophile on the carbonyl group carbon becomes more and more difficult, due to **steric hinderance** (crowding) i.e. **as the crowding increases, the reactivity of carbonyl group compound decreases,** so the reactivity of formaldehyde is more as there is no alkyl group, while the other aldehydes having one alkyl group the reactivity is less compared to formaldehyde while ketones having two alkyl groups, the reactivity is less than the corresponding aldehydes.

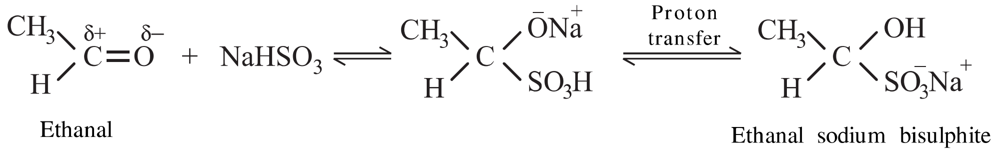
(ii) Inductive effect : The attachment of nucleophile on the carbonyl group depends upon the magnitude of the positive charge on the carbonyl carbon. The alkyl group **electron donating and hence has inductive effect (+I effect).** So more the number of alkyl groups on carbonyl carbon, **the magnitude of the positive charge on carbonyl carbon decreases,** which lowers the reactivity towards nucleophilic addition reactions. Therefore formaldehyde is **more reactive** compared to other aldehydes and ketones which are less reactive than aldehydes.

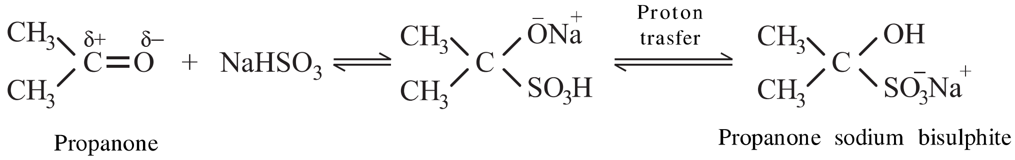
The aromatic aldehydes and ketones are **less reactive** than aliphatic aldehydes and ketones because the electron-donating resonance effect of benzene ring which **increases the electron density on carbonyl carbon,** hence it gets repelled by the nucleophiles. The aromatic aldehyde (like benzaldehyde) is more reactive than alkyl aryl ketone (like acetophenone) while diaryl ketones (like benzophenone) is less reactive than alkyl aryl ketone.

Nucleophilic addition reactions :

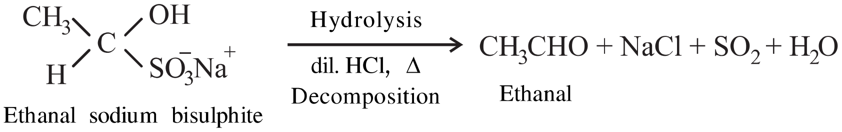
(i) Addition of sodium hydrogen sulphite ($NaHSO_3$) : Due to less steric hindrance most of the aldehydes and aliphatic methyl ketones, react with sodium hydrogen sulphite and form additive compounds, while the acetophenone does not react.

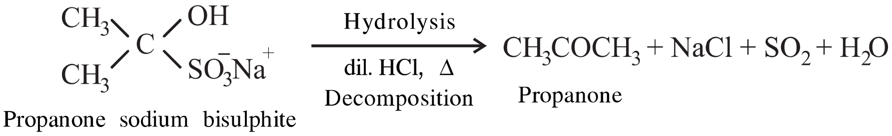






The proton transfer equilibrium lies more towards the **right side for most of the aldehydes and to the left side for most of the ketones.** The bisulphite product obtained, are usually crystalline solids. If they are heated with dilute mineral acids or aqueous alkalies they decompose, due to hydrolysis and regenerate the original aldehyde or ketone.

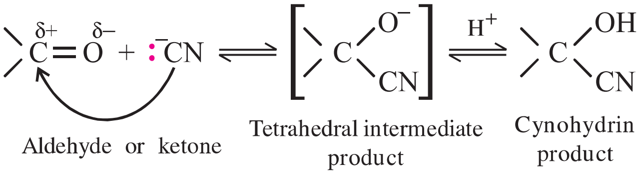


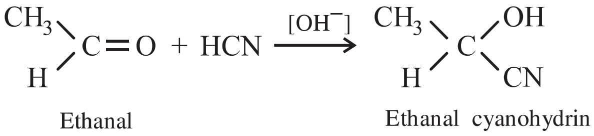


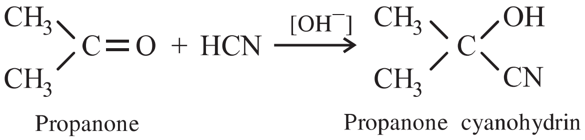
Therefore, this reaction is useful for separation and purification of aldehydes and ketones from non-carbonyl compounds.

(ii) Addition of Hydrogen cyanide (HCN) : The aldehydes and ketones react with hydrogen cyanide and give product cyanohydrins. The reaction is extremely slow and so it is carried out in **presence of base which acts as a catalyst.** The reaction occurs very slowly with pure HCN but in presence of base (as a catalyst) the $:^{-}CN$ is generated which is a stronger nucleophile and gets added readily to carbonyl compounds and the product cyanohydrin is obtained. For example,

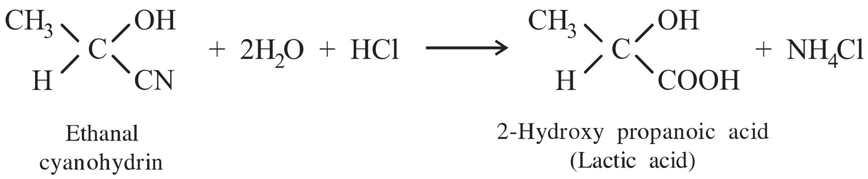
$$HCN + OH^- \rightleftharpoons :\bar{C}N + H_2O$$





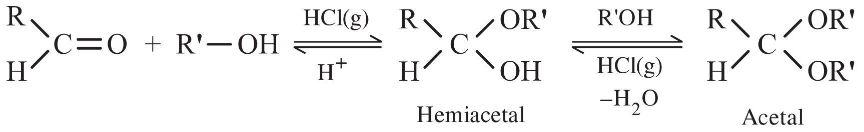


Cyanohydrins are important synthetic substances because they can be readily hydrolysed to give 2-hydroxy acids.

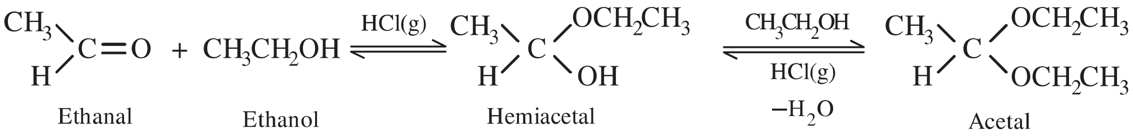


(iii) Addition of Grignard reagent : Aldehydes and ketones react with Grignard reagent to form nucleophilic addition compounds. This intermediate product upon hydrolysis with water or dilute mineral acid gives 1^0, 2^0 or 3^0 alcohols. This you have studied in unit 7 of Semester III.

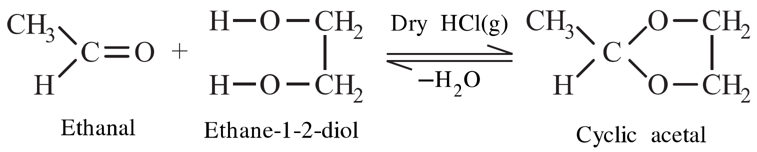
(iv) Addition of alcohols : Aldehyde reacts with one equivalent of monohydric alcohol in presence of dry hydrogen chloride to yield alkoxy alcohol intermediate known **as hemi acetal** (hemi means half). Being unstable it immediately reacts with one more molecule of alcohol to form stable gem-di alkoxy compound **known as acetal.**



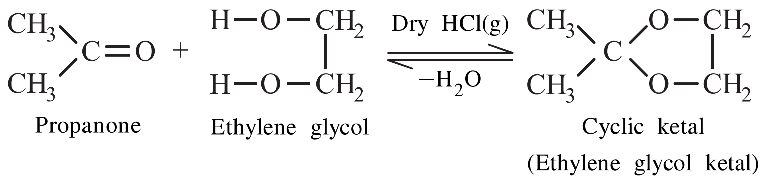
Dry hydrogen chloride protonates the oxygen of aldehyde (carbonyl compound) hence the density of positive charge on carbonyl carbon increases i.e. the electropositivity of carbonyl carbon increases, which **facilitates the nucleophilic attachment.** Dry HCl gas absorbs the water molecules which is produced during acetal formation and shifts the equilibrium in the forward direction. For example,



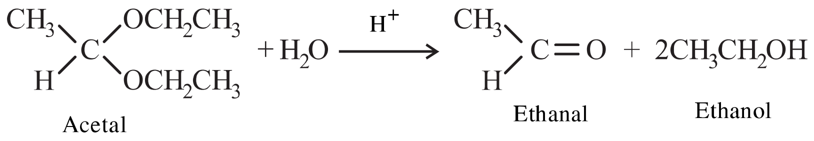
Instead of two molecules of monohydric alcohol in presence of dry hydrogen chloride or paratoluene sulphonic acid (PTS), one molecule of dihydric alcohol such as ethane-1, 2-diol (ethylene glycol) is used, then cyclic acetal (ethylene glycol-acetal) is formed.

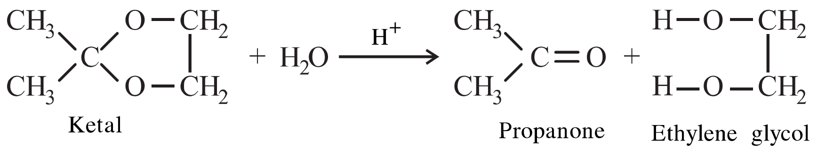


Ketones do not react with monohydric alcohols but react with dihydric alcohols in presence of dry hydrogen chloride or PTS and give **cyclic ketals.** For example,



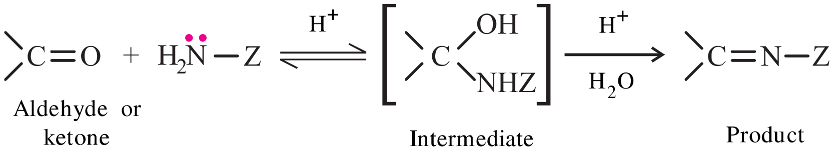
In the formation of acetals and ketals the reactions are reversible; so they are decomposed by dilute acid and the aldehydes and ketones are regenerated. For example,





Nucleophilic addition reactions followed by elimination of a molecule of water :

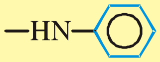
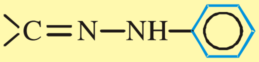
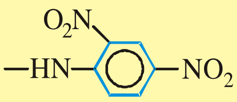
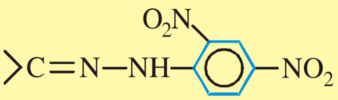
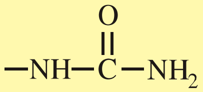
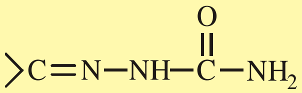
(v) Addition of ammonia and its derivatives : Aldehydes and ketones react with ammonia $(\ddot{N}H_3)$ and its derivatives $(H_2\ddot{N}-Z)$. The reaction is catalysed by acid, hence the carbonyl groups gets protonated, so the positive charge on carbonyl carbon is increased and as a result the weak nucleophile like ammonia and its derivatives readily attach to the carbonyl group. For example,



The equilibrium favours the product formation due to rapid dehydration of the intermediate to form $\rangle C=N-Z$. The $\ddot{N}H_3$ and its N–substituted derivatives and product are given in table 5.4

Table 5.4 Some N-Substituted Derivatives of Aldehydes and Ketones

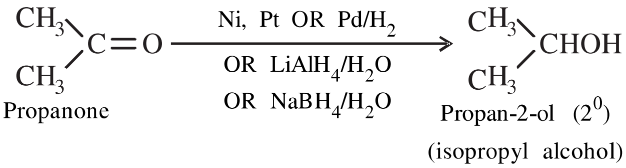
Z	Reagent's name	Carbonyl derivative	Product's name
–H	Ammonia	$\rangle C=NH$	Imine
–R	Amine	$\rangle C=NR$	Substituted imine (Schiff's base)
–OH	Hydroxylamine	$\rangle C=N-OH$	Oxime

$-NH_2$	Hydrazine	$>C=N-NH_2$	Hydrazone
	Phenylhydrazine		Phenylhydrazone
	2,4-Dinitrophenyl hydrazine		2,4-Dinitrophenyl hydrazone
 $-NH-\overset{\overset{O}{\parallel}}{C}-NH_2$	Semicarbazide	 $>C=N-NH-\overset{\overset{O}{\parallel}}{C}-NH_2$	Semicarbazone

Reduction reactions of aldehydes and ketones :

(i) Reduction to alcohols : Aldehydes and ketones on **reduction give 1^0 and 2^0 alcohols** respectively. Reduction is carried out either catalytically with H_2 in presence of Ni, Pt or Pd or chemically by lithium aluminium hydride ($LiAlH_4$) or sodium borohydride ($NaBH_4$). $LiAlH_4$ is a much more powerful reducing agent than $NaBH_4$.

$$\underset{\text{Methanal}}{HCHO} \xrightarrow[\text{OR } LiAlH_4/H_2O \text{ OR } NaBH_4/H_2O]{\text{Ni, Pt OR Pd}/H_2} \underset{\text{Methanol } (1^0)}{CH_3OH}$$



(ii) Reduction to hydrocarbons : The carbonyl group of aldehydes or ketones is reduced to **methylene ($-CH_2-$) group** to form hydrocarbon by using different reducing agents.

(a) Wolff-Kishner reduction : Aldehyde or ketone is heated with hydrazine (NH_2NH_2) and KOH in high boiling solvent like ethylene glycol which results **into formation of hydrocarbon.** For example,

$$\underset{\text{Ethanal}}{CH_3CHO} \xrightarrow[-H_2O]{NH_2NH_2} CH_3CH{=}NNH_2 \xrightarrow[\text{KOH } 453\text{-}473 \text{ K}]{\text{Ethylene glycol}} \underset{\text{Ethane}}{CH_3CH_3} + N_2$$

$$\underset{\text{Propanone}}{CH_3COCH_3} \xrightarrow[4[H] \text{ Ethylene-glycol } 453\text{-}473 \text{ K}]{NH_2NH_2, \text{ KOH}} \underset{\text{Propane}}{CH_3CH_2CH_3} + H_2O + N_2$$

(b) Clemmensen reduction : Aldehyde or ketone is **reduced to hydrocarbon,** on treatment with zinc amalgam and concentrated hydrochloric acid. For example,

$$\underset{\text{Ethanal}}{CH_3CHO} + 4[H] \xrightarrow[\text{Con. HCl}]{\text{Zn-Hg}} \underset{\text{Ethane}}{CH_3CH_3} + H_2O$$

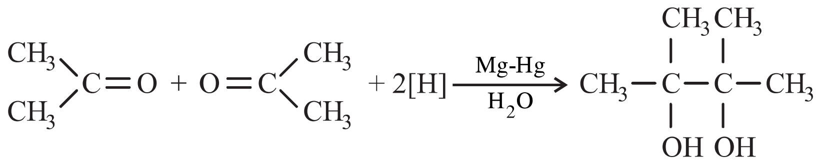
$$\underset{\text{Propanone}}{CH_3COCH_3} + 4[H] \xrightarrow[\text{Con. HCl}]{\text{Zn-Hg}} \underset{\text{Propane}}{CH_3CH_2CH_3} + H_2O$$

(c) Reduction with HI and Red P : Aldehyde or ketone when heated with hydroiodic acid and red phosphorus **is reduced to hydrocarbon.** For example,

$$\underset{\text{Ethanal}}{CH_3CHO} + 4HI \xrightarrow[423\ K]{\text{Red P}} \underset{\text{Ethane}}{CH_3CH_3} + H_2O + 2I_2$$

$$\underset{\text{Propanone}}{CH_3COCH_3} + 4HI \xrightarrow[423\ K]{\text{Red P}} \underset{\text{Propane}}{CH_3CH_2CH_3} + H_2O + 2I_2$$

(iii) Reduction to pinacols (Bimolecular reduction) : Ketones on reduction with magnesium amalgam and water form **pinacol.** For example,



Propanone

Propanone

2, 3-Dimethyl-butane-2,3-diol

(Pinacol)

Oxidation of aldehydes and ketones : Aldehydes are easily oxidized to carboxylic acids containing the same number of carbon atoms, because of the presence of hydrogen atom on carbonyl group which is converted to –OH group, without involving the cleavage of any other bond. So they easily **get oxidized by both strong and weak oxidizing agent.** While ketones can be oxidized by powerful oxidizing agent only, because during oxidation carbon-carbon bond cleavage results into mixture of carboxylic acids, each containing less number of carbon atoms than the original ketone. The mild oxidizing agents given below are used to distinguish aldehydes from ketones.

Oxidation of aldehydes :

(i) Tollens' test : Aldehyde and freshly prepared ammoniacal silver nitrate solution (Tollens' reagent) when gently warmed, the aldehyde is oxidized to carboxylate ion, Tollens' reagent is reduced to metallic silver which gets deposited on the inner wall of test-tube giving shining surface like mirror. Hence this test is also **known as silver mirror test.** Aromatic and aliphatic aldehydes are both oxidized by Tollens' reagent. **In laboratory the aldehydes can be detected by Tollens' test.**

$$RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \rightarrow RCOO^- + \underset{\text{Silver mirror}}{2Ag} + 4NH_3 + 2H_2O$$

(ii) Fehling's test : Fehling solution A ($CuSO_4$ solution) and Fehling solution B (alkaline solution of sodium potassium tartarate-Rochelle salt) are mixed in equal proportion and the mixture is heated with aldehyde, gives **red precipitate of cuprous oxide.** This test is **known as Fehling's test.** This test is only for aliphatic aldehydes because the **aromatic aldehydes are not reduced by the Fehling solution. In laboratory the aldehydes can be detected by Fehling's test.**

$$RCHO + 2Cu^{2+} + 5OH^- \xrightarrow{\Delta} RCOO^- + \underset{\text{Red ppts}}{Cu_2O} + 3H_2O$$

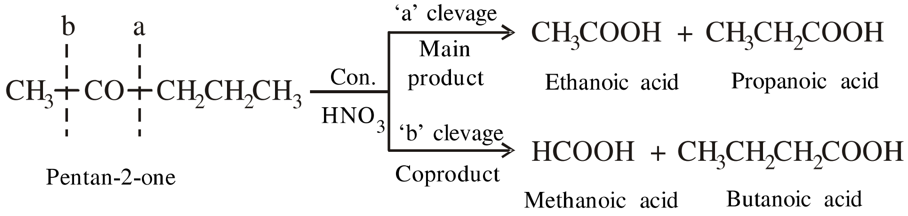
(iii) Benedict's test : This test is similar to Fehling's test but instead of tartarate ions the citrate ions were used. The reaction is same and this test is also not given by aromatic aldehydes.

Oxidation of ketones :

(i) By strong oxidizing agents : The ketones are oxidized by strong oxidizing agents like con. HNO_3, $KMnO_4 / H_2SO_4$, $K_2Cr_2O_7 / H_2SO_4$ etc. and give mixture of carboxylic acids. **Symmetrical ketones give mixture of two carboxylic acids.** For example,

$$\underset{\text{Propanone}}{CH_3COCH_3} + 3[O] \xrightarrow[+ H_2SO_4]{K_2Cr_2O_7} \underset{\text{Ethanoic acid}}{CH_3COOH} + \underset{\text{Methanoic acid}}{HCOOH} \xrightarrow{[O], \Delta} \underset{\text{Ethanoic acid}}{CH_3COOH} + CO_2 + H_2O$$

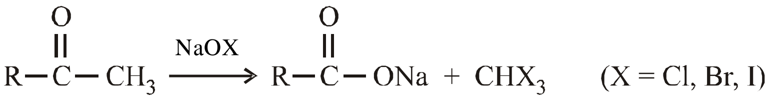
Unsymmetrical ketone gives mixture of four carboxylic acids. For example,



In case of unsymmetrical ketones, the keto group stays preferentially with the smaller alkyl group and is the main product and this is known as Popoff's rule.

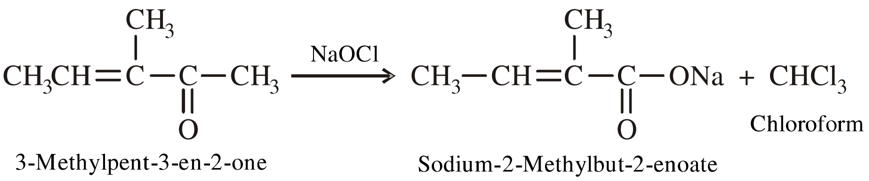
(ii) Oxidation with sodium hypohalide (NaOX or X_2 + NaOH) (Iodoform test) :

Aldehydes or ketones containing CH_3CO- group, when treated with an excess of halogen in presence of alkali give haloform. For Example,



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow{NaOX} R-\overset{\overset{\displaystyle O}{\|}}{C}-ONa + \underset{\text{Haloform}}{CHX_3} \quad (X = Cl, Br, I)$$

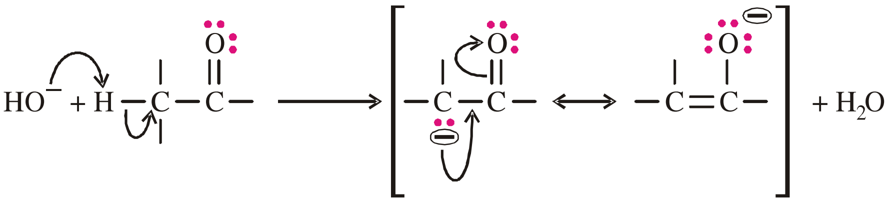
During halo formation reaction, if carbon-carbon double bond is present in the molecules, the double bond is not oxidized; hence, double bond remains unaffected. For example,



$$\underset{\text{3-Methylpent-3-en-2-one}}{CH_3CH=\overset{\overset{\displaystyle CH_3}{|}}{C}-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3} \xrightarrow{NaOCl} \underset{\text{Sodium-2-Methylbut-2-enoate}}{CH_3-CH=\overset{\overset{\displaystyle CH_3}{|}}{C}-\underset{\underset{\displaystyle O}{\|}}{C}-ONa} + \underset{\text{Chloroform}}{CHCl_3}$$

Reaction due to α–hydrogen of aldehydes and ketones :

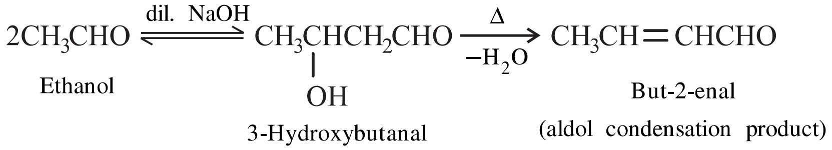
The hydrogen atoms present on the carbon atom next to the carbonyl group of aldehydes and ketones are called α–hydrogen atoms, and the acidity of α–hydrogen atom is due to electron with-drawing, inductive effect of the carbonyl group and also due to resonance stabilization of the conjugate base (enolate ion).



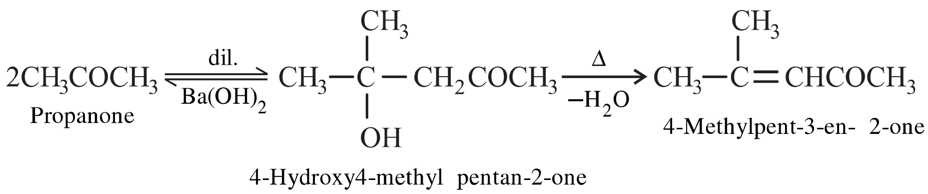
Carbanion   Enolate ion

Due to acidity of α–hydrogen of aldehydes and ketones, they undergo a number of reactions such as aldol condensation, cross aldol condensation etc.

(i) Aldol condensation : In this reaction, two same molecules of an aldehyde or ketone, having **atleast one α–hydrogen atom** undergo a reaction in presence of dilute alkali (dil. NaOH, Na_2CO_3, $Ba(OH)_2$ etc.) to form β–hydroxy aldehyde (Aldol) or β–hydroxy ketone (Ketol) respectively. This reaction is **known as aldol condensation reaction.** The name aldol is derived from the name of two functional groups aldehyde and alcohol present in the product. Same way ketol is derived from two functional groups of ketone and alcohol present in the product. The aldol and ketol readily lose water molecule to give α–β unsaturated carbonyl compounds which are aldol condensation product and the reaction is called aldol condensation. For example,



$$\underset{\text{Ethanol}}{2CH_3CHO} \overset{\text{dil. NaOH}}{\rightleftharpoons} \underset{\text{3-Hydroxybutanal}}{CH_3\underset{\underset{OH}{|}}{C}HCH_2CHO} \xrightarrow[-H_2O]{\Delta} \underset{\substack{\text{But-2-enal}\\ \text{(aldol condensation product)}}}{CH_3CH=CHCHO}$$

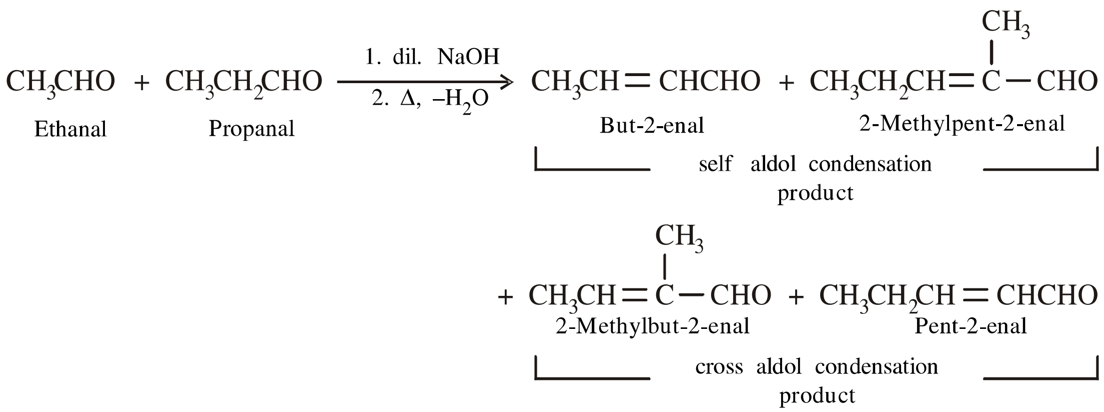


$$\underset{\text{Propanone}}{2CH_3COCH_3} \underset{Ba(OH)_2}{\overset{\text{dil.}}{\rightleftharpoons}} \underset{\text{4-Hydroxy4-methyl pentan-2-one}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2COCH_3} \xrightarrow[-H_2O]{\Delta} \underset{\text{4-Methylpent-3-en- 2-one}}{CH_3-\overset{\overset{CH_3}{|}}{C}=CHCOCH_3}$$

Formaldehyde, benzaldehyde and benzophenone do not undergo aldol condensation since they do not have an α–hydrogen atom.

(ii) Cross-aldol condensation : An aldol condensation between **two different aldehydes or two different ketones or between one aldehyde and one ketone is called cross aldol condensation** and gives mixture of four products which are difficult to separate. So cross aldol condensations are of little synthetic value. However, if one carbonyl compound does not possess α–hydrogen atom then cross aldol condensations are of great synthetic utility. e.g.,

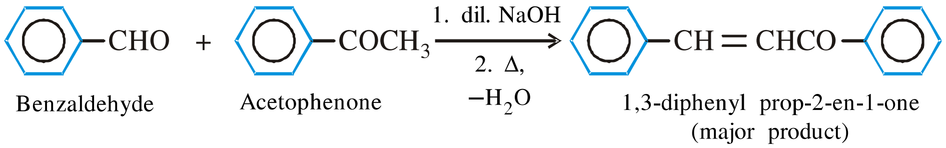
(I)



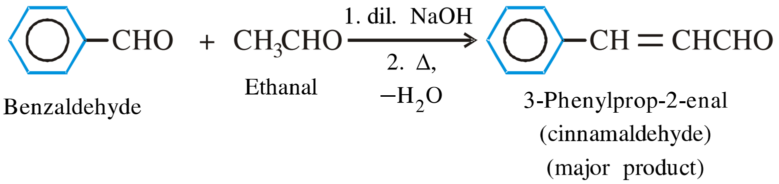
$$\underset{\text{Ethanal}}{CH_3CHO} + \underset{\text{Propanal}}{CH_3CH_2CHO} \xrightarrow[\text{2. }\Delta,\ -H_2O]{\text{1. dil. NaOH}} \underbrace{\underset{\text{But-2-enal}}{CH_3CH=CHCHO} + \underset{\text{2-Methylpent-2-enal}}{CH_3CH_2CH=\overset{\overset{CH_3}{|}}{C}-CHO}}_{\text{self aldol condensation product}}$$

$$+ \underbrace{\underset{\text{2-Methylbut-2-enal}}{CH_3CH=\overset{\overset{CH_3}{|}}{C}-CHO} + \underset{\text{Pent-2-enal}}{CH_3CH_2CH=CHCHO}}_{\text{cross aldol condensation product}}$$

(II)

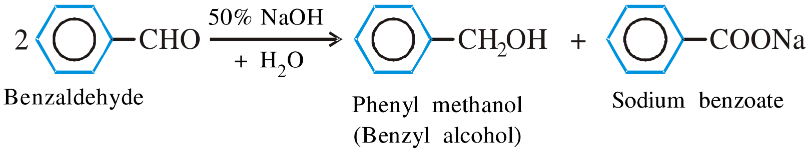


1,3-diphenyl prop-2-en-1-one
(major product)

(III) 

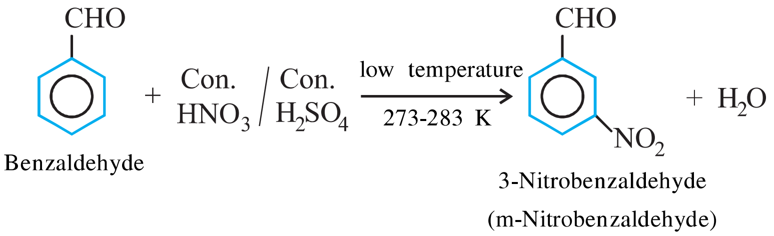
(iii) Cannizzaro reaction : Aldehydes which do not have an α–hydrogen atom, when treated with concentrated alkali solution, undergo **disproportionation,** i.e., self-oxidation and reduction occur. One molecule of aldehyde is reduced to the corresponding alcohol, at the cost of the other molecule of aldehyde which is oxidized to the corresponding carboxylic acid salts. This reaction is called **Cannizzaro** reaction. For example,

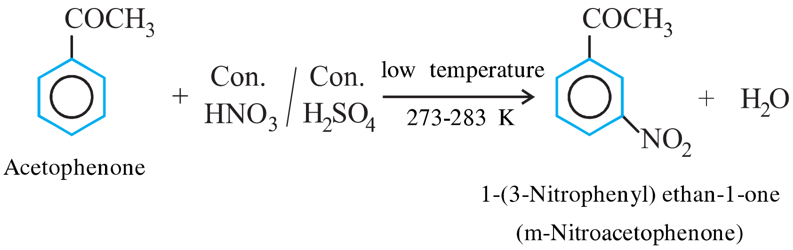
$$\underset{\text{Methanal}}{2HCHO} \xrightarrow[\text{or con. KOH} \; + H_2O]{50\ \%\ \text{NaOH}} \underset{\text{Methanol}}{CH_3OH} + \underset{\text{Sodium formate}}{HCOONa} \ (\text{or} \ HCOOK)$$



Electrophilic substitution reactions of aromatic aldehydes and ketones :

Nitration : Aromatic aldehydes and ketones undergo the electrophilic substitution reactions of the benzene nucleus. Since the aldehyde and ketone functional groups are electron withdrawing groups and so act as deactivating group and hence act as meta-directing group. So substitution occurs at meta-position. For example,





Substitution reactions like halogenation, sulphonation also occur at m-position.

5.5 Uses of Aldehydes and Ketones

In chemical industry, aldehydes and ketones are used as solvents, starting materials and reagents, for the synthesis of other products. **Formaldehyde** is used in manufacturing of bakelite, resins and other polymers. A 40% solution of formaldehyde in water is called **formalin** which is used for the preservation of dead bodies of animals of biological or anatomical specimens. It is also used as a disinfectant and germicide. Formaldehyde is used in leather industry. Acetaldehyde is used for giving the shining like silver to mirror. Benzaldehyde is used as a flavouring agent in perfume industry and is also used in manufacturing of dye like malachite green. Acetone is used in manufacturing liquid nail polish and also as nail polish remover. Acetone and methylethyl ketone are common industrial solvents. Some aldehydes and ketones for example butyraldehyde, vanillin, acetophenone, camphor etc. are well-known for their odours and flavours.

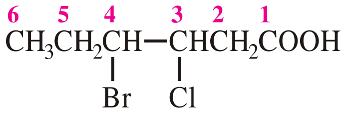
5.6 Corboxylic Acids

Organic compounds containing –COOH as the functional group are called carboxylic acids. The –COOH group is made up of a carbonyl group ($>C=O$) and hydroxyl group (–OH). So 'Carb' from carbonyl and 'oxyl' from hydroxyl, hence –COOH is called carboxyl group. The –COOH attaches to aliphatic alkyl (or hydrogen atom) or aromatic group, and according to that it may be aliphatic or aromatic carboxylic acid. Aliphatic or aromatic carboxylic acids have one or more than one –COOH groups. A large number of carboxylic acids are found in nature. Higher numbers (C_{12} to C_{18}) of aliphatic acids occur in nature known **as fatty acids,** which occur in natural fats as triesters of glycerol. Carboxylic acid serves as starting material for preparing a number of other important compounds such as acid chloride, acid anhydride, ester, amide etc.

5.7 Common and IUPAC Nomenclature of Carboxylic Acids

The common names of some aliphatic carboxylic acids are derived from the Greek or Latin names of their natural sources (Plant or animal product) from which they were first isolated. For example, formic acid was first obtained by distillation of red ants (Latin : formica means red ant). The acetic acid (Latin: acetum means vinegar). The butyric acid (Latin : butyrum means butter) and caprylic, caproic and capric acids (Latin : caper means goat).

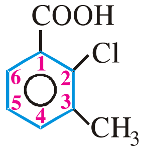
The IUPAC names of the saturated monocarboxylic acids are given by replacing the ending alphabet -'e' in the name of the corresponding hydrocarbon with the suffix **'-oic acid'.** For the naming of substituted and branched chain acids, select the –COOH group containing longest chain. The positions of the substituents are indicated by **numbering the carboxylic carbon as number one.** For Example,



$$\overset{6}{C}H_3\overset{5}{C}H_2\underset{Br}{\overset{4}{C}H}-\underset{Cl}{\overset{3}{C}H}\overset{2}{C}H_2\overset{1}{C}OOH$$

4-Bromo-3-chlorohexanoic acid

The IUPAC names of aromatic monocarboxylic acids are derived by benzene carboxylic acid or benzoic acid and the position of the substituents are indicated by **number with carbon atom carrying** –COOH group being numbered one. For example,



The IUPAC name is 2-Chloro-3-methyl benzene carboxylic acid

OR

2-Chloro-3-methylbenzoic acid

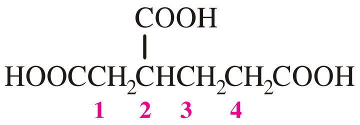
Aliphatic or aromatic carboxylic acid **having more than one –COOH** groups are named as di, tri, tetra... and polycarboxylic acids, according to two, three, four.... and many carboxyl groups present in respective molecules. In case of aliphatic dicarboxylic acids the position of –COOH groups are not indicated, but in case of aromatic dicarboxylic acid and other carboxylic acids, the position of the –COOH groups are indicated by the number and the numbers are indicated before the multiplicative prefix. **The ending -'e' of the hydrocarbon is retained in carboxylic acid having more than one** –COOH groups. For example,

$$\begin{matrix}\text{COOH}\\ |\\ \text{COOH}\end{matrix}$$

Ethane dioic acid

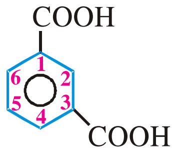
$HOOCCH_2CH_2CH_2COOH$

Pentane dioic acid



$$\begin{matrix} & & \text{COOH} & & \\ & & | & & \\ \text{HOOCCH}_2 & & \text{CHCH}_2 & \text{CH}_2 & \text{COOH}\\ 1 & & 2 & 3 & 4\end{matrix}$$

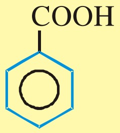
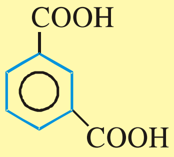
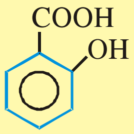
Butane-1,2,4-tricarboxylic acid



Benzene-1,3-dicarboxylic acid

Common and IUPAC names of some carboxylic acids are given in table 5.5.

Table 5.5 Names and Structures of Some Carboxylic Acids

Structure	Common name	IUPAC name
$HCOOH$	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3CH_2COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2COOH$	Butyric acid	Butanoic acid
$(CH_3)_2CHCOOH$	Isobutyric acid	2-Methylpropanoic acid
$HOOC–COOH$	Oxalic acid	Ethanedioic acid
$HOOC–CH_2COOH$	Malonic acid	Propanedioic acid
$HOOC–(CH_2)_2–COOH$	Succinic acid	Butanedioic acid
$HOOC–(CH_2)_3–COOH$	Glutaric acid	Pentanedioic acid
$HOOC–(CH_2)_4–COOH$	Adipic acid	Hexanedioic acid
$HOOC–CH_2–CH(COOH)CH_2COOH$	–	Propane-1,2,3-tricarboxylic acid
	Benzoic acid	Benzenecarboxylic acid OR Benzoic acid
	Isophthalic acid	Benzene-1,3-dicarboxylic acid
	Salicylic acid	2-Hydroxybenzenecarboxylic acid OR 2-Hydroxybenzoic acid

5.8 Structure of Carboxylic Group

In carboxylic acid compounds the carbon atom of carboxyl group is attached to one oxygen atom by single bond and another by double bond, but **electron and neutron diffraction studies** have proved that –COOH has planar structure having angle of about 120^0, so the two oxygen atoms are sp^2

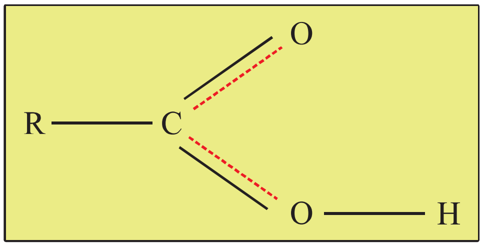


Fig 5.6

hybridised. The π electrons of double bond are delocalized between carbon and oxygen bond as shown in figure 5.6.

Here, σ and π bond between carbon and oxygen, carbon and both oxygen atoms are sp^2 hybridised R–C–O and O–C–O angle 120^0.

5.9 Methods of Preparation of Carboxylic Acids

Some important general methods of preparation of carboxylic acid are as follows :

(i) From primary alcohols and aldehydes : The primary alcohols are readily oxidized to the corresponding carboxylic acids with common oxidizing agents such as $KMnO_4$ in **neutral, acidic or alkaline medium** or by $K_2Cr_2O_7$ or CrO_3 (chromium trioxide) in acidic medium. Oxidation with $K_2Cr_2O_7$ or CrO_3 in acidic medium often give some amount of esters. Therefore the oxidation with $KMnO_4$ is preferred. Under these conditions the potassium salts of the carboxylic acid is first obtained, which on treatment with dil H_2SO_4 gives carboxylic acids. For example,

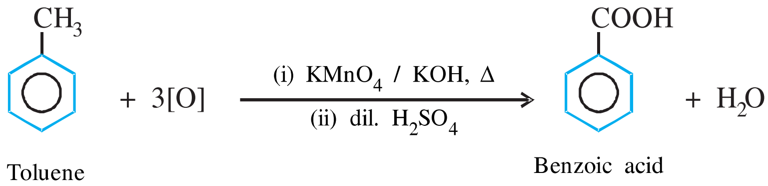
$$\underset{\text{Ethanol}}{3CH_3CH_2OH} + 4KMnO_4 \rightarrow \underset{\substack{\text{Potassium}\\\text{ethanoate}}}{3CH_3COOK} + KOH + 4MnO_2 + 4H_2O$$

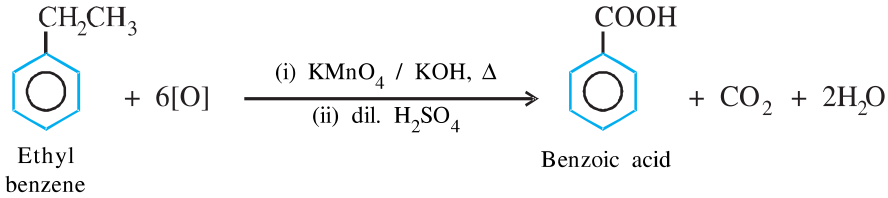
$$\underset{\substack{\text{Potassium}\\\text{ethanoate}}}{2CH_3COOK} + H_2SO_4 \rightarrow \underset{\text{Ethanoic acid}}{2CH_3COOH} + K_2SO_4$$

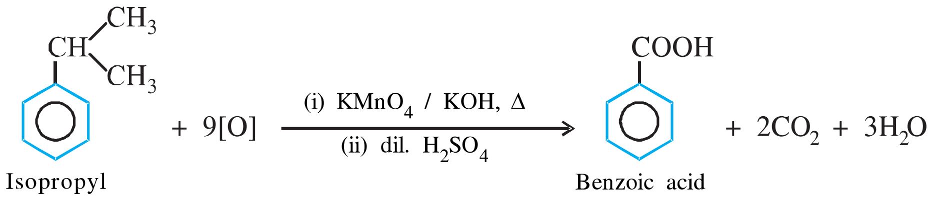
$$\underset{\text{Heptanol}}{CH_3(CH_2)_6OH} \xrightarrow{CrO_3\ /\ H_2SO_4} \underset{\text{Heptanoic acid}}{CH_3(CH_2)_5COOH}$$

Aldehydes are easily oxidized to corresponding carboxylic acids with $KMnO_4$ in neutral, acidic or alkaline medium or by $K_2Cr_2O_7$ or CrO_3 in acidic medium and also even with mild oxidizing agent such as Tollens' reagent which is discussed in unit 5.4.

(ii) From alkylbenzene and alkenes : Aromatic carboxylic acids are prepared by the vigorous oxidation of alkylbenzene with acidic or alkaline $KMnO_4$ or acidified $K_2Cr_2O_7$ (chromic acid) or dil. HNO_3. During these oxidation the entire side chain is oxidized to carboxylic acid group irrespective of the length of the side chain. **1^0 and 2^0 alkyl groups are oxidized in this manner but the 3^0 alkyl group is not oxidized and remains unaffected.** For example,

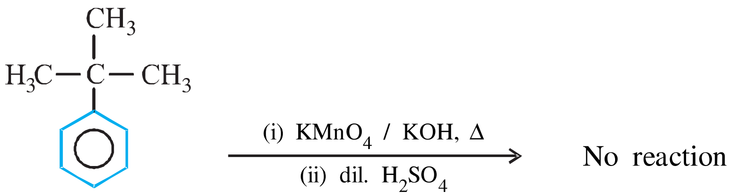






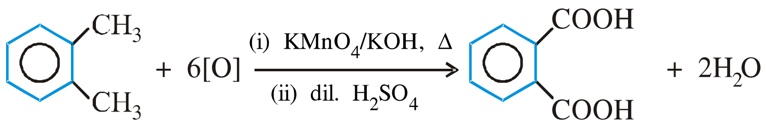
Isopropyl benzene

Benzoic acid



Tert-butylbenzene

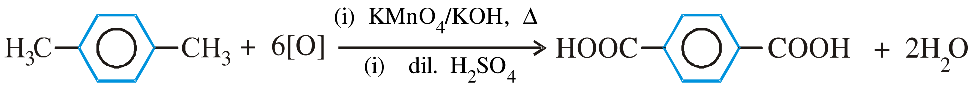
If there are two or more than two alkyl groups in benzene ring, each group is oxidized to –COOH group. For example,



1,2-Dimethylbenzene

(o-Xylene)

Benzene-1,2-dicarboxylic acid



1,4-Dimethylbenzene

(p-Xylene)

Benzene-1,4-dicarboxylic acid

Substituted alkenes are also oxidized to carboxylic acid by acidic $K_2Cr_2O_7$ or alkaline $KMnO_4$. For example,

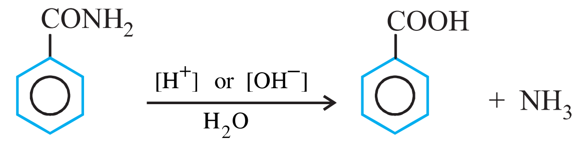
$$CH_3\text{–}CH{=}CH\text{–}CH_3 \xrightarrow[\text{(ii) dil. } H_2SO_4]{\text{(i) } KMnO_4 \text{ / KOH, } \Delta} 2CH_3COOH$$

But-2-ene Ethanoic acid

(iii) From nitriles and amides : Nitriles are hydrolysed to amide and then to carboxylic acid on boiling with mineral acids or alkalies as a catalyst. For example,

$$CH_3CN \xrightarrow[H_2O]{[H^+] \text{ or } [OH^-]} CH_3CONH_2 \xrightarrow[\Delta]{[H^+] \text{ or } [OH^-]} CH_3COOH + NH_3$$

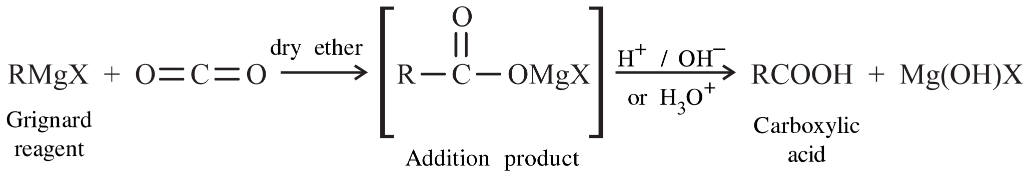
Ethane nitrile Ethanamide Ethanoic acid



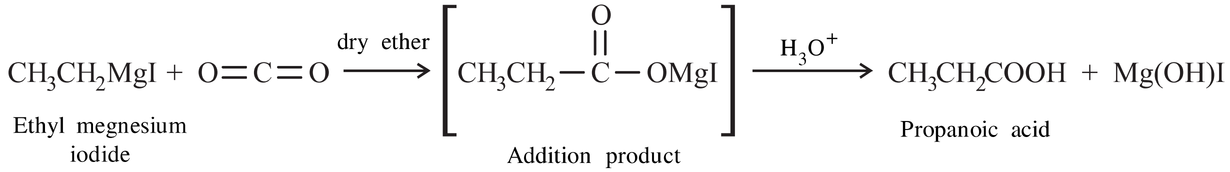
Benzamide

Benzoic acid

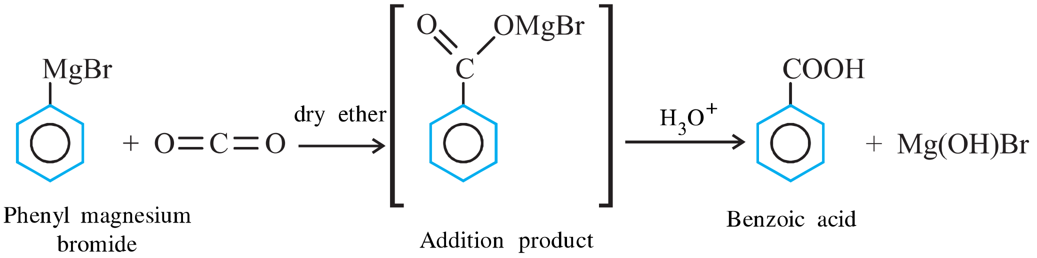
(iv) From Grignard reagent : Carboxylic acids can be prepared by bubbling CO_2 gas into the etheral solution of a suitable Grignard reagent or by adding the solution of Grignard reagent to crushed dry ice (solid CO_2) suspended in ether. First the addition product is obtained, which on decomposition with mineral acid gives carboxylic acid. For example,



$$RMgX + O{=}C{=}O \xrightarrow{\text{dry ether}} \left[R-\overset{\overset{O}{||}}{C}-OMgX\right] \xrightarrow[\text{or } H_3O^+]{H^+ / OH^-} RCOOH + Mg(OH)X$$

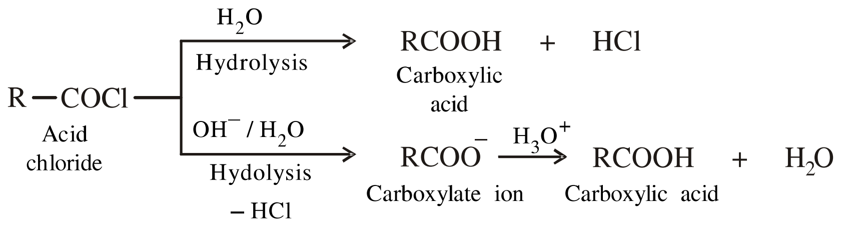


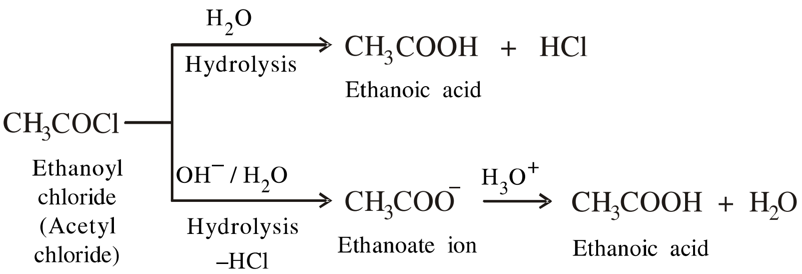
$$CH_3CH_2MgI + O{=}C{=}O \xrightarrow{\text{dry ether}} \left[CH_3CH_2-\overset{\overset{O}{||}}{C}-OMgI\right] \xrightarrow{H_3O^+} CH_3CH_2COOH + Mg(OH)I$$



In both the methods-nitriles and Grignard reagent are useful for converting the alkyl halide to the carboxylic acid, having carbon atom or atoms more than that present in alkyl halide.

(v) From acid chloride and anhydrides : Acid chloride when hydrolysed by water gives carboxylic acid, and more readily hydrolysed with aqueous alkali to give carboxylate ions, which on acidification gives corresponding carboxylic acids. For example,



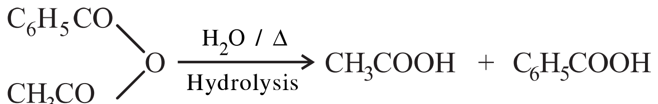


Anhydrides on hydrolysis with water gives carboxylic acids. For example,

$$(CH_3CO)_2O \xrightarrow[\text{Hydrolysis}]{H_2O / \Delta} 2CH_3COOH$$

Ethanoic anhydride (Acetic anhydride) — Ethanoic acid

$$\underset{\text{Benzoic anhydride}}{(C_6H_5CO)_2O} \xrightarrow[\text{Hydrolysis}]{H_2O\,/\,\Delta} \underset{\text{Benzoic acid}}{2C_6H_5COOH}$$



$$\underset{\text{Benzoic ethanoic anhydride}}{(C_6H_5CO)(CH_3CO)O} \xrightarrow[\text{Hydrolysis}]{H_2O\,/\,\Delta} \underset{\text{Ethanoic acid}}{CH_3COOH} + \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

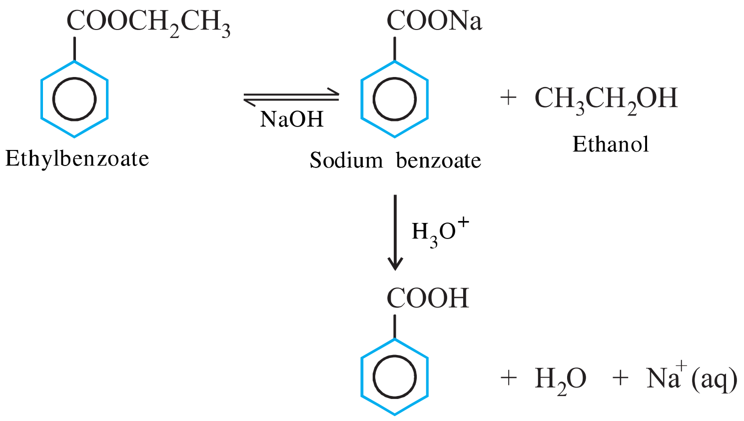
(vi) From ester : Hydrolysis of esters in presence of mineral acids give carboxylic acids directly while hydrolysis in presence of alkali gives carboxylates, which on acidification give corresponding carboxylic acid. For example,

$$\underset{\text{Ethylethanoate}}{CH_3COOCH_2CH_3} \overset{H_3O^+}{\rightleftharpoons} \underset{\text{Ethanoic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{CH_3CH_2OH}$$

$$\underset{\text{Ethylethanoate}}{CH_3COOCH_2CH_3} \overset{NaOH}{\rightleftharpoons} \underset{\text{Sodium ethanoate}}{CH_3COONa} + \underset{\text{Ethanol}}{CH_3CH_2OH}$$

$$\Big\downarrow H_3O^+$$

$$\underset{\text{Ethanoic acid}}{CH_3COOH} + Na^+(aq) + H_2O$$



Ethylbenzoate

Sodium benzoate

Ethanol

Benzoic acid

5.10 Physical Properties of Carboxylic Acids

The first three aliphatic acids (C_1 to C_3) are colourless liquids with pungent smell. The next three (C_4 to C_6) are colourless oily liquids with unpleasant smell and remaining three (C_7 to C_9) are colourless liquids with unpleasant smell at room temperature, while carboxylic acids with ten or more carbon atoms are colourless, waxy solids with no distinct smell due to low volatality. Aromatic carboxylic acids are solid with no distinct smell. C_1 to C_4 aliphatic carboxylic acids are fairly soluble in water, while C_5 and C_6 are slightly soluble and remaining are insoluble in water. The aromatic acids are almost insoluble in cold water, but soluble in hot water. The solubility of lower members of aliphatic carboxylic acids is due to hydrogen bond formation. The hydrogen bonding of carboxylic acid is stronger than that of alcohol, so the melting points and boiling points of carboxylic acids are more than those of alcohols