POLYMERS AND PRACTICAL ORGANIC CHEMISTRY NOTES

→ The term polymer is used to describe a very large molecule that is made up of many small repeating molecular units. These small molecular units from which the polymer is formed are called monomers.

→ The chemical reaction that joins the monomers together is called polymerisation.

→ Starting from n molecules of a compound M, linking in a linear manner will form polymer $x–M–(M)_{n-2}–M–y$. The nature of linkages at the terminal units i.e. M – x and M – y depends upon the mode of reaction used in making the polymers.

Homopolymers and Copolymers

Polymers which are formed by only one type of monomer are called homopolymers. Some examples of homopolymers and their monomers are given below :

Homopolymer	Monomer
Starch	Glucose
Cellulose	Glucose
Glycogen	Glucose
Dextrin	Glucose
Inulin	Fructose
Polyethylene	Ethylene
Polyvinyl chloride	Vinyl chloride
Teflon	Tetrafluoro ethylene
Nylon–6	Caprolactam
Polystyrene	Styrene
Orlon (Acrilan)	Acrylonitrile
Plexiglas (Lucite)	Methyl methaacrylate
Polyvinyl acetate	Vinyl acetate

Polymers, which are formed by more than one type of monomers are known as copolymers. Some examples are given below in the table :

Copolymer	Monomers
Saran	Vinyl chloride and vinylidene chloride
SAN	Styrene and acrylonitrile
ABS	Acrylonitrile, butadiene and styrene
Butyl rubber	Isobutylene and Isoprene
Buna–S, SBR	Styrene and Butadiene
Buna–N, NBR	Acrylonitrile and Butadiene
Nylon–66	Hexamethylenediamine and Adipic acid
Terylene	Terephthalic acid and ethylene glycol

Types of copolymers

Depending upon the distribution of monomer units, the following types of copolymers are possible.

(1) Random Copolymer

If the monomer units have random distribution throughout the chain, it is called random copolymer. For example, if the monomer A and monomer B undergo copolymerisation then the structure of the random copolymer is

$$nA + nB \longrightarrow -A-A-B-A-B-B-A-B-A-A-A-B-$$

segment of random copolymer

(2) Alternating Copolymer

If the two monomer units present alternatively throughout the polymer chain, it is said to be alternating copolymer. For example,

$$nA + nB \longrightarrow -A-B-A-B-A-B-$$

segment of alternating copolymer

The exact distribution depends upon the proportion of the two reactant monomers and their relative reactivities. In practice neither perfectly random nor perfectly alternating copolymers are usually formed. However, most copolymers tend more towards alternating type but have many random imperfections.

(3) Block copolymer

Polymers in which different blocks of identical monomer units alternate with each other are called block copolymers.

For example,

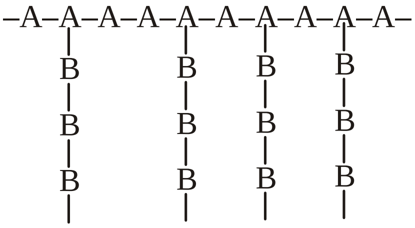
$$-B-B-A-A-A-A-A-A-B-B-B-B-B-B-A-A-$$

segment of a block polymer

Block copolymer can be prepared by initiating the radical polymerisation of one monomer to grow homopolymer chains, followed by addition of an excess of the second monomer.

(4) Graft copolymer

Polymers in which homopolymer branches of one monomer unit are grafted onto a homopolymer chain of another monomer unit are called graft co–polymers. For example:



(Segment of a graft copolymer)

Graft copolymers are prepared by γ-irradiation of a homopolymer chain in the presence of a second monomer. the high energy radiation knock out H-atoms from the homopolymer chain at random points thus generating radical sites that can initiate polymerisation of the second monomer.

CLASSIFICATION OF POLYMERS

Polymers are classified in following ways :

(I) CLASSIFICATION BASED UPON SOURCE

(1) Natural polymers

Polymers which are obtained from animals and plants are known as natural polymers. Examples of natural polymers are given below.

Natural polymer	**Monomers**
1. Polysaccharide	Monosaccharide
2. Proteins	α-L-Amino acids
3. Nucleic acid	Nucleotide
4. Silk	Amino acids
5. Natural Rubber (cis polyisoprene)	Isoprene (2-Methyl-1,3-butadiene)
6. Gutta purcha (trans polyisoprene)	Isoprene

Natural polymers which take part in metabolic processes are known as biopolymers. Examples are polysaccharides, proteins, RNA and DNA.

(2) Semisynthetic polymers

Polymers which are prepared from natural polymers are known as semisynthetic polymers. Most of the semisynthetic polymers are prepared from cellulose. Examples are: cellulose acetate, cellulose nitrate, cellulose xanthate and Rayon.

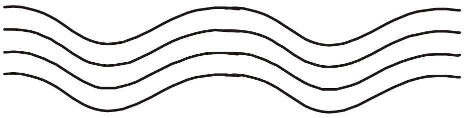
(3) Synthetic polymers

Man-made polymers, i.e. polymers prepared in laboratory are known as synthetic polymers. Example are : PVC, polyethylene, polystyrene, nylon-6, nylon-66, nylon-610, terylene, synthetic rubbers etc.

(II) CLASSIFICATION BASED UPON SHAPE

(1) Linear polymers

Polymer whose structure is linear is known as linear polymer. The various linear polymeric chains are stacked over one another to give a well packed structure.



The chains are highly ordered with respect to one another. The structure is close packed in nature, due to which they have high densities, high melting point and high tensile (pulling) strength. Linear polymers can be converted into fibres.

Note :

(i) All fibers are linear polymers. Examples are cellulose, silk, nylon, terylene etc.

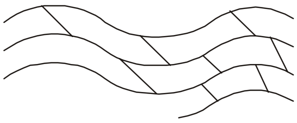
(ii) Linear polymers may be condensation as well as addition polymers. Examples are cellulose, polypeptide, nucleic acid, nylon, terylene etc.

(2) Branched chain polymers

Branched chain polymers are those in which the monomeric units constitute a branched chain. Due to the presence of branches, these polymers do not pack well. As a result branched chain polymers have lower melting points, low densities and tensile strength as compared to linear polymers. Branched chain polymers may be formed due to addition as well as condensation polymerisation. Examples are amylopectin, glycogen, low density polyethylene.

(3) Cross-linked or Three Dimensional network polymers

In these polymers the initially formed linear polymeric chains are joined together to form a three dimensional network structure. These polymers are hard, rigid and brittle. Cross-linked polymers are always condensation polymers. Resins are cross linked polymers, Urea-formaldehyde resin, phenol-formaldehyde resin.

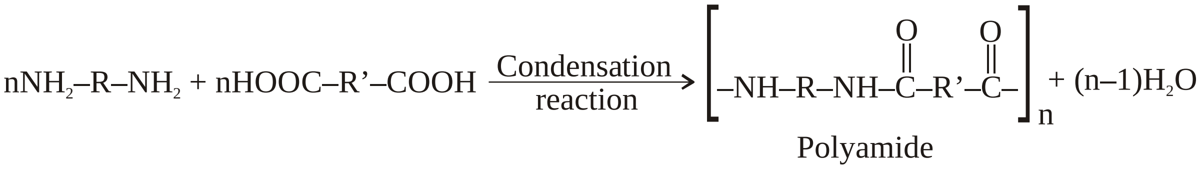


CLASSIFICATION BASED UPON SYNTHESIS

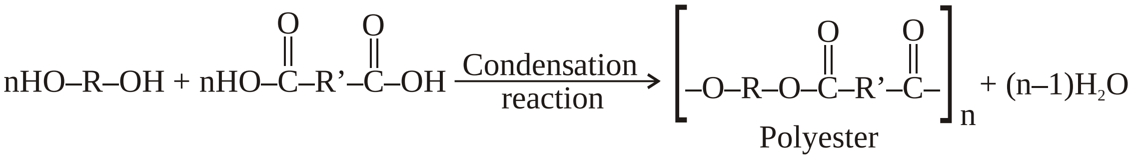
(1) Condensation polymerisation

They are formed due to condensation reactions. Condensation polymerisation is also known as step growth polymerisation. For condensation polymerisation, monomers should have at least two functional groups. Both functional groups may be same or different. Monomers having only two functional group always give linear polymer.

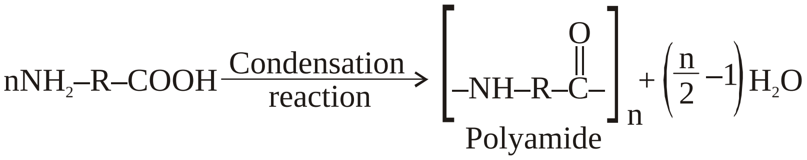
For example,



$$nNH_2{-}R{-}NH_2 + nHOOC{-}R'{-}COOH \xrightarrow[\text{reaction}]{\text{Condensation}} \underset{\text{Polyamide}}{\left[-NH{-}R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}R'{-}\overset{\overset{O}{\|}}{C}{-}\right]_n} + (n-1)H_2O$$



$$nHO{-}R{-}OH + nHO{-}\overset{\overset{O}{\|}}{C}{-}R'{-}\overset{\overset{O}{\|}}{C}{-}OH \xrightarrow[\text{reaction}]{\text{Condensation}} \underset{\text{Polyester}}{\left[-O{-}R{-}O{-}\overset{\overset{O}{\|}}{C}{-}R'{-}\overset{\overset{O}{\|}}{C}{-}\right]_n} + (n-1)H_2O$$

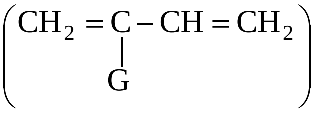


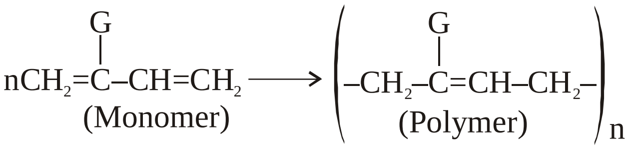
$$nNH_2{-}R{-}COOH \xrightarrow[\text{reaction}]{\text{Condensation}} \underset{\text{Polyamide}}{\left[-NH{-}R{-}\overset{\overset{O}{\|}}{C}{-}\right]_n} + \left(\frac{n}{2}-1\right)H_2O$$

Condensation polymers do not contain all atoms initially present in the monomers. Some atoms are lost in the form of small molecules. Monomer having three functional groups always gives cross-linked polymer.

Examples are : Urea-formaldehyde resin, phenol-formaldehyde resin.

(3) Addition polymerisation

Polymers which are formed by addition reaction are known as addition polymers. If monomer is ethylene or its derivative, then addition polymer is either linear polymer of branch- chain polymer. Examples are : polystyrene, polytetrafluoroethylene, polyacrylonitrile etc. If monomer is 1, 3-butadiene or 2-substituted-1, 3-butadiene  $\left(CH_2=\underset{\displaystyle G}{\underset{|}{C}}-CH=CH_2\right)$, then polymer is always branched chain polymer.



$$nCH_2{=}\overset{\displaystyle G}{\overset{|}{C}}{-}CH{=}CH_2 \longrightarrow \left(-CH_2{-}\overset{\displaystyle G}{\overset{|}{C}}{=}CH{-}CH_2{-}\right)_n$$

(Monomer) (Polymer)

(Monomer)	**(Polymer)**
(i) G = H : 1,3 - Butadiene	(i) Polybutadiene
(ii) G = CH_3 ; 2 - Methyl-1,3-butadiene or isoprene	(ii) Polyisoprene
(iii) G = Cl ; 2 -Chloro-1,3-butadiene or chloroprene	(ii) Plychloroprene (Neoprene)

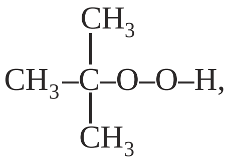
Addition polymers retain all the atoms of the monomer units in the polymer. Addition polymerisation takes place in three steps. Initiation, chain propagation and chain termination. Addition polymers are called as chain growth polymers.

Types of Addition Polymerisation

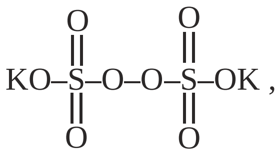
(A) Radical Polymerisation :

Radical polymerisaiton takes place in the presence of radical initiators. The radical initiator may be any of the following :

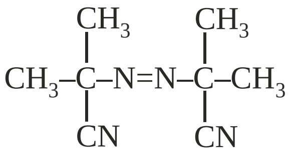
H_2O_2,



$$CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}O{-}O{-}H,$$



$$KO{-}\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{||}{\underset{||}{S}}}}{-}O{-}O{-}\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{||}{\underset{||}{S}}}}{-}OK\ ,$$



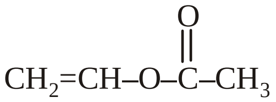
$$CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CN}{\overset{|}{\underset{|}{C}}}}{-}N{=}N{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CN}{\overset{|}{\underset{|}{C}}}}{-}CH_3$$

Reaction intermediate of radical polymerizaiton is a free radical. Radical polymerization has more chance for those monomers whose free radicals are more stable.

Examples are :

$C_6H_5{-}CH{=}CH_2$,
Styrene

$CH_2{=}CH{-}Cl$,
Vinyl chloride

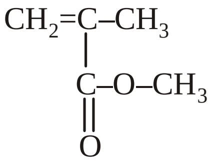


$$CH_2{=}CH{-}O{-}\overset{\displaystyle O}{\overset{||}{C}}{-}CH_3$$

Vinyl acetate

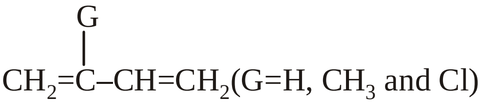
$CH_2{=}CH{-}CN$

Acrylonitrile
(vinyl cyanide)



$$CH_2{=}\underset{\displaystyle \underset{\displaystyle \underset{\displaystyle O}{||}}{C}{-}O{-}CH_3}{\underset{|}{C}}{-}CH_3$$

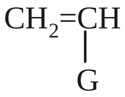
Methyl methacrylate



$$CH_2{=}\overset{\displaystyle G}{\overset{|}{C}}{-}CH{=}CH_2(G{=}H,\ CH_3 \text{ and } Cl)$$

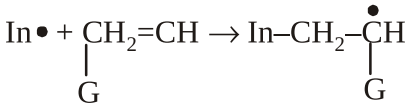
2-substituted-1,3-butadiene

Radical polymer has linear as well as branched chain structure.

Most of the commercial addition polymers are vinyl polymers obtained from alkenes and their derivatives  $\mathrm{CH_2{=}\underset{\underset{\displaystyle G}{|}}{CH}}$ [G is H, C_6H_5 ,R etc.]. This type of polymerisation is preformed by heating the monomer with only a very small amount of the initiator or by exposing the monomer to light. the general mode of radical polymerisation of vinyl monomers is depicted below :

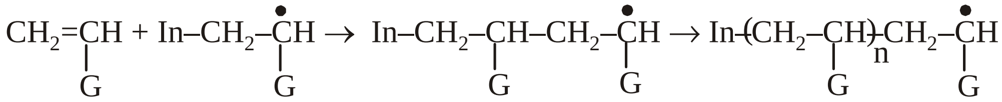
Chain initiation step :

Initiator $\rightarrow$ In $\bullet$



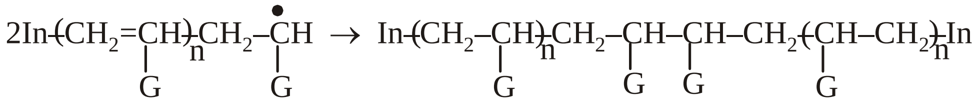
$$\mathrm{In^{\bullet} + \underset{\underset{\displaystyle G}{|}}{C}H_2{=}CH \rightarrow In{-}CH_2{-}\underset{\underset{\displaystyle G}{|}}{\overset{\bullet}{C}}H}$$

Chain propagating step :



$$\mathrm{CH_2{=}\underset{\underset{\displaystyle G}{|}}{C}H + In{-}CH_2{-}\underset{\underset{\displaystyle G}{|}}{\overset{\bullet}{C}}H \rightarrow In{-}CH_2{-}\underset{\underset{\displaystyle G}{|}}{C}H{-}CH_2{-}\underset{\underset{\displaystyle G}{|}}{\overset{\bullet}{C}}H \rightarrow In{+}(CH_2{-}\underset{\underset{\displaystyle G}{|}}{C}H{+})_n CH_2{-}\underset{\underset{\displaystyle G}{|}}{\overset{\bullet}{C}}H}$$

Chain terminating step :

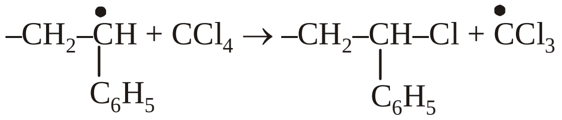


$$\mathrm{2In(CH_2{=}\underset{\underset{\displaystyle G}{|}}{C}H)_n CH_2{-}\underset{\underset{\displaystyle G}{|}}{\overset{\bullet}{C}}H \rightarrow In(CH_2{-}\underset{\underset{\displaystyle G}{|}}{C}H)_n CH_2{-}\underset{\underset{\displaystyle G}{|}}{C}H{-}\underset{\underset{\displaystyle G}{|}}{C}H{-}CH_2(\underset{\underset{\displaystyle G}{|}}{C}H{-}CH_2)_n In}$$

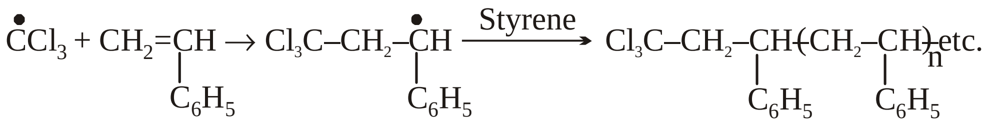
Polymer

In vinylic polymerisation, various other reaction of free radicals with some other compounds present may compete with the parent addition chain reactions. One such reaction takes place with molecules that can react with the growing chain to interrupt the further growth. This leads to the lowering of the average molecular mass of the polymer. Such reagents are called as chain transfer agents and include CCl_4, CBr_4 etc.

For example, in the presence of CCl_4, styrene polymerises to form polystyrene of a lower average molecular mass which also contains some chlorine what happens here is that growing polystyrene radical which normally would add on a monomer reacts with the chain transfer agent to end the original chain and produces a new radical. The latter initiates a new polymerisation chain and thereby forms a new polymer as depicted below.



$$\mathrm{{-}CH_2{-}\underset{\underset{\displaystyle C_6H_5}{|}}{\overset{\bullet}{C}}H + CCl_4 \rightarrow {-}CH_2{-}\underset{\underset{\displaystyle C_6H_5}{|}}{C}H{-}Cl + \overset{\bullet}{C}Cl_3}$$



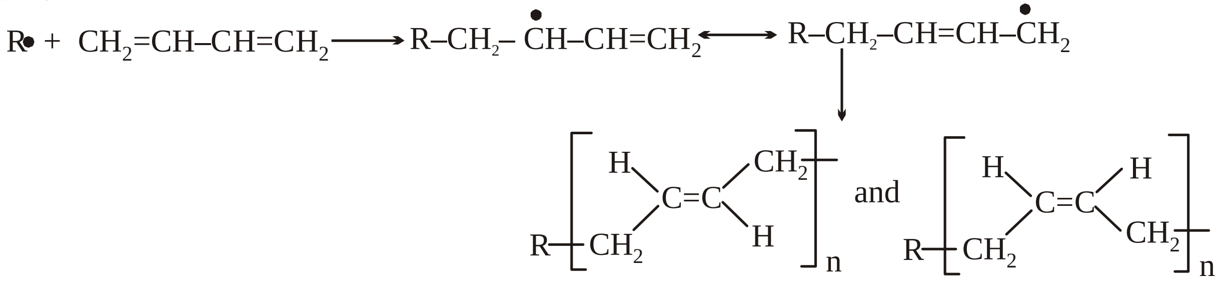
$$\mathrm{\overset{\bullet}{C}Cl_3 + CH_2{=}\underset{\underset{\displaystyle C_6H_5}{|}}{C}H \rightarrow Cl_3C{-}CH_2{-}\underset{\underset{\displaystyle C_6H_5}{|}}{\overset{\bullet}{C}}H \xrightarrow{\text{Styrene}} Cl_3C{-}CH_2{-}\underset{\underset{\displaystyle C_6H_5}{|}}{C}H(CH_2{-}\underset{\underset{\displaystyle C_6H_5}{|}}{C}H)_n\ etc.}$$

If the chain transfer agent a radical, which is highly unreactive, the reaction chain gets terminated such a compound thus inhibits or arrests polymerisation. Many amines, phenols, quinones etc. act as inhibitors. So, even traces of certain impurities, which can act as chain transfer agent or an inhibitor can interfere with the original polymerisation chain reaction. Hence, the monomers could be free from such inhibitors.

In case the alkene is a (diene), the following kinds of polymerisation is possible :

(1) 1,4 - polymerisaiton.

When the polymerisation takes place at C_1 and C_4 of butadiene, an unbranched polymer is formed. This product is different from that formed from an alkene having a double bond, which at each of its carbons is substituted by different groups and hence can exist either as trans-polybutadiene or cis-polybutadiene or a mixture as shown below.



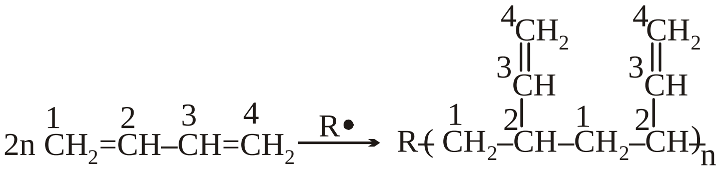
$$R\bullet + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow R{-}CH_2{-}\dot{C}H{-}CH{=}CH_2 \longleftrightarrow R{-}CH_2{-}CH{=}CH{-}\dot{C}H_2$$

trans-1,4 structure

cis -1,4 structure

(2) 1,2-Polymerisation

Alternatively, 1,3 -butadiene can undergo polymerisaiton at C_1 and C_2 to yield the polymeric product, polyvinly polythene.



$$2n\ \overset{1}{C}H_2{=}\overset{2}{C}H{-}\overset{3}{C}H{=}\overset{4}{C}H_2 \xrightarrow{R\bullet} R{-}\!\left(\overset{1}{C}H_2{-}\overset{2}{C}H(\overset{3}{C}H{=}\overset{4}{C}H_2){-}\overset{1}{C}H_2{-}\overset{2}{C}H(\overset{3}{C}H{=}\overset{4}{C}H_2)\right)_n$$

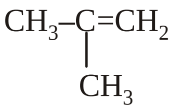
The double bonds in these initial polymers can be linked by further treatment with chemicals to modify the properties of the polymers. These reactions form the basis of the formation of rubber.

(B) Cationic Polymerisation :

Polymerisation which is initiated by an electrophile is known as cationic polymerisation. Reaction intermediate of cationic polymerisation is a carbocation. Carbocations can undergo rearrangement leading to the formation of a more stable carbocation. The electrophile commonly used for initiation is $BF_3.OEt_2$. Monomers that are best able to undergo polymerisation by a cationic mechanism are those with electron - donating substituents that can stabilise the carboncation. Some examples are:

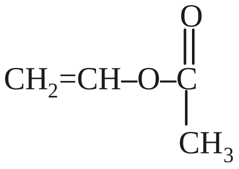
$CH_2{=}CH{-}CH_2$

Propene



$CH_3{-}C(CH_3){=}CH_2$

Isobutene



$CH_2{=}CH{-}O{-}C({=}O){-}CH_3$

Vinyl acetate

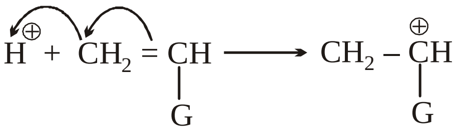
$C_6H_5{-}CH{=}CH_2$

Styrene

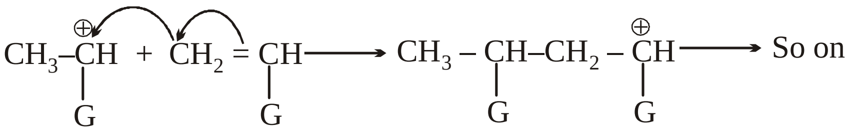
It is terminated by a base.

Thus, when the initiator is cationic in nature, it would generate a cationic intermediate on addition to the double bond for propagating the addition chain process and is termed as cationic addition polymerisation. The process is initiated by an acid. The stages of polymerisation are depicted below.

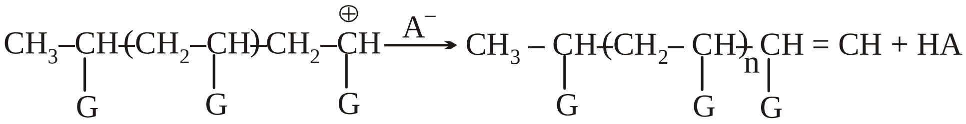
Chain initiation step :



Chain propagating step :

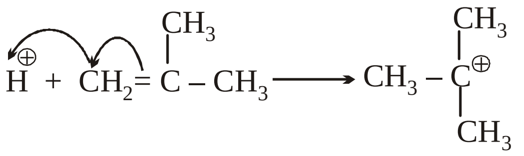


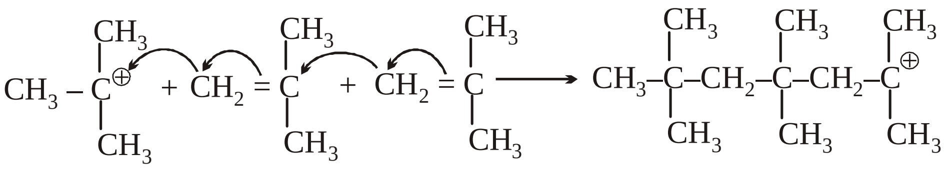
Chain terminating step :



$$CH_3-\underset{G}{CH}(CH_2-\underset{G}{CH})CH_2-\overset{\oplus}{\underset{G}{CH}} \xrightarrow{A^-} CH_3-\underset{G}{CH}(CH_2-\underset{G}{CH})_n\underset{G}{CH}=CH + HA$$

Cationic polymerisation is facilitated in monomers containing electron - releasing groups. Thus, isobutylene undergoes cationic polymerisation easily as it has two electron releasing $-CH_3$ groups that will stabilize the intermediate carbocation.





(Butyl Rubber)

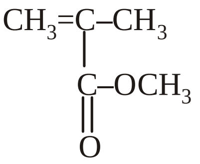
(C) Anionic Polymerisation :

Anionic polymerisation takes place in the presence of base or nucleopile, which is initiator in this polymerization. Reaction intermediate in propagation steps are carboanion. The suitable initiator can be $NaNH_2$ or RLi. Those monomers undergo anionic polymerisation reaction whose anion is stable.

Example of monomers are :

$CH_2=CH-Cl$
Vinyl chloride

$CH_2=CH-CN$
Acrylonitrile



$$CH_3-\underset{\underset{\underset{O}{\|}}{C-OCH_3}}{C}=CH_2$$

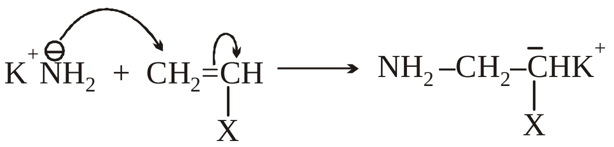
Methyl methacrylate

$C_6H_5-CH=CH_2$
Styrene

Anionic polymerisation always gives linear polymer. Anionic polymerisation termnated by an acid.

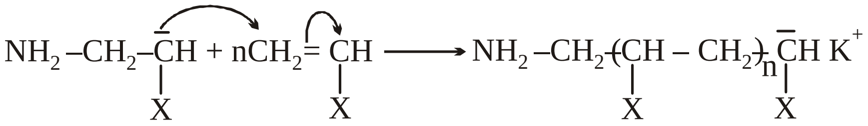
The formation of polystyrene from styrene in the presence of potassium amide is an important example of this category of polymerisation. The mode of anionic polymerisation is depicted below:

Chain initiation step :



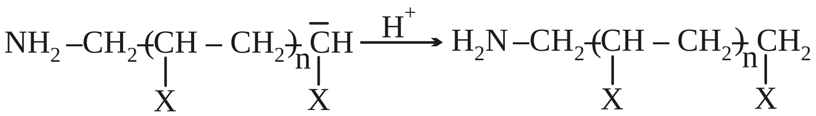
$$\overset{+}{K}\,\overset{\ominus}{N}H_2 + CH_2{=}\underset{X}{CH} \longrightarrow NH_2-CH_2-\underset{X}{\bar{C}}HK^+$$

Chain propagating step :



$$NH_2-CH_2-\underset{X}{\bar{C}}H + nCH_2{=}\underset{X}{CH} \longrightarrow NH_2-CH_2-(\underset{X}{CH}-CH_2)_n-\underset{X}{\bar{C}}H\,K^+$$

Chain terminating step :



$$NH_2-CH_2-(\underset{X}{CH}-CH_2)_n-\underset{X}{\bar{C}}H \xrightarrow{H^+} H_2N-CH_2-(\underset{X}{CH}-CH_2)_n-\underset{X}{CH_2}$$

(D) Ziegler- Natta polymerisation :

Addition polymerisation which takes place in the presence of Ziegler- Natta catalyst [$(C_2H_5)_3Al$ and $TiCl_4$] is known as Ziegler- Natta polymerisation or coordination polymersation. Ziegler- Natta polymerisation always gives linear, stereo-regular polymers. Ziegler- Natta catalyst revolutionised the field of polymer chemistry because they allow the synthesis of stronger and stiffer polymers (due to linear geometry) that have greater resistance to cracking and heat.

High density polyethylene is prepared using a Ziegler- Natta catalyst.

CLASSIFICATION BASED ON INTERMOLECULAR FORCES (SECONDARY FORCES)

Intermolecular forces present between polymeric chains are (a) Van der waals forces (b) Hydrogen bonds and (c) Dipole - dipole attractions. Mechanical properties such as tensile strength, elasticity, toughness etc. depend upon the secondary forces present between the polymeric chains. Magnitude of secondary forces depends upon the size of the molecule and the number of functional groups along the polymeric chains. Magnitude of secondary forces is directly proportional to the length of the polymeric chain. On the basis of magnitude of secondary forces, polymers can be divided into the following following categories.

(1) Elastomes

An elastomer is a plastic that stretches and then reverts back to its original shape. It is randomly oriented amorphous polymer. It must have some cross-links so that the chains do not slip over one another. Very weak Vander Waal forces are present in between polymeric chains.

When elastomers are stretched , the random chains stretch out, but there are insufficient Vander Waal forces to maintain them in that configuration and position. When the stretching force is removed, they go back to their random shape. Elastomers have the ability to stretch out over ten times their normal length. Important examples are vulcanized rubbers.

Note : Addition polymers obtained from butadiene and its derivatives are elastomers.

(2) Fibres

Fibres are linear polymers in which the individual chains of a polymer are held together by hydrogen bonds or dipole-dipole attraction. In the fibres, the polymeric chains are highly ordered with respect to one another. Due to strong intermolecular forces of attraction and highly ordered geometry, fibres have high tensile strength and least elasticity. they have crystalline character and have high melting points and low solubility. Examples are cellulose, nylon, terylene, wool, silk etc.

Note :

(i) Condensation polymers formed from bifunctional monomers are fibres in character.

(ii) Addition polymers of alkene derivatives having strong- I group are fibres in character.

(3) Thermoplastic Polymers

Thermoplastic polymers are polymers that have both ordered crystalline regions (the regions of the polymer in which the chains are highly ordered with respect to one another) and amorphous, non crystalline regions (the regions of the polymer in which the chains are randomly oriented. The intermolecular forces of attraction are in between elastomers and fibres. There are no cross links between the polymeric chains. Thermoplastic polymers are hard at room temperature, but when they are heated, the individual chains can slip past one another and the polymer become soft and viscous. this soft and viscous material become rigid on cooling. The process of heating softening and cooling can be repeated as many times as desired without any change in chemical composition and mechanical properties of the plastic. As a result, these plastics can be moulded into toys, buckets, telephone and television cases. Some common examples are : polyethene, polypropylene, polystyrene, polyvinyl chloride, teflon etc.

Note : Addition polymers obtained from ethylene and ethylene derivatives are thermoplastic polymers.

(4) Thermosetting Polymers

Polymers which become hard on heating are called thermosetting polymers. thermosetting polymers can be heated only once when it permanently sets into a solid, which cannot be remelted by heating. Thermosetting polymers are cross- linked polymers . Greater the degree of cross - linking that exist, the more rigid is the polymer. Cross-linking reduces the mobility of the polymer chains, causing them to be relatively brittle materials. the hardening on heating is due to the extensive cross-linking between different polymer chains to give a three dimensional network solid. Examples are : phenol formaldehyde resin, urea-formaldehyde resin ,melamine - formaldehyde resin.

DIFFERENCE BETWEEN THERMOPLASTIC AND THERMOSETTING POLYMERS

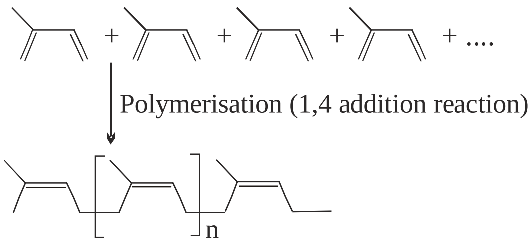
S.No.	Thermoplastic polymers	Thermosetting polymers
1.	Soften and melt on heating and become hard on cooling i.e. process is reversible	Become hard on heating and process is irreversible.
2.	Can be moulded and remoulded and reshaped.	They can be moulded once and cannot be remoulded or reshaped.
3.	They are addition polymers	They are condensation polymers.
4.	Structure is generally linear	Structure is cross - linked.

RUBBER

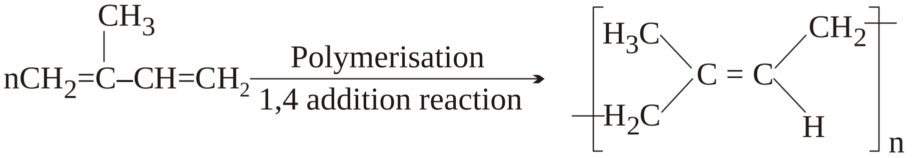
1. Natural Rubber

Natural rubber is obtained from nearly five hundred different plants but the main source is a braziliensis tree. It is obtained in the form of milky sap known as latex. This latex is coagulated with acetic acid and formic acid. The coagulated mass is then squeezed.

The raw natural rubber is a soft gummy and sticky mass.It is insoluble in water, dilute acids and alkalies but soluble in non-polar solvents. It has low elasticity and low tensile strength. Natural rubber is a polymer of 2-methyl-1,3-butadiene(isoprene). On average, a molecule of rubber contains 5000 isoprene units held together by head to tail. All the double bonds in rubber are cis, hence natural rubber is cis-polyisoprene.

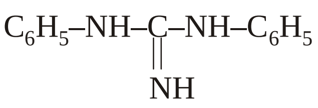


Gutta - percha is a naturally occurring isomer of rubber in which all the double bonds trans. Thus, gutta-percha is trans-polyisoprene.



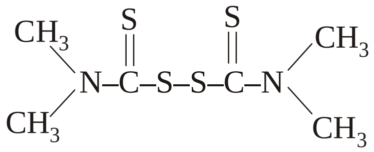
It is harder and more brittle than rubber. It is the filling material that dentists use in root canal treatment.

In order to give strength and elasticity to natural rubber, it is vulcanized. Heating of rubber with sulphur or sulphur containing compound at 150° C for few hours is known as vulcanisation. The essential feature of the vulcanisation is the formation of cross-linking between the polymeric chains. This cross-linking gives mechanical strength to the rubber. Vulcanisation process can be enhanced in the presence of certain organic compounds known as accelerators. The common accelerators are:



$$C_6H_5{-}NH{-}\underset{\underset{NH}{\|}}{C}{-}NH{-}C_6H_5$$

Diphenyl guanidine



Tetramethylthioureadisulph

In addition, fillers such as carbon black and zinc oxide are usually added to the crude rubber before vulcanisation in order to improve its wearing characteristics.

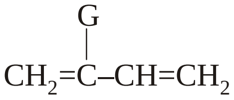
Natural rubber is used for making shoes, water - proof coats and golf balls. Vulcanised rubber is used for manufacture of rubber bands, gloves tubing and car tyres.

SYNTHETIC RUBBER OR POLYMERISATION OF DIENES

Polymers of 1,3 - butadienes are called synthetic rubbers because they have some of the properties of natural rubbers including the fact that they are water proof and elastic. Synthetic rubbers have some improved properties. They are more flexible, tougher and more durable than natural rubber.

1. **Homopolymers**

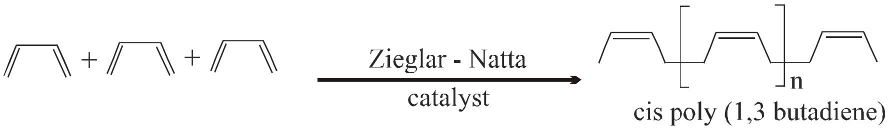
Monomer of this class is 2 - substituted - 1,3- butadienes.



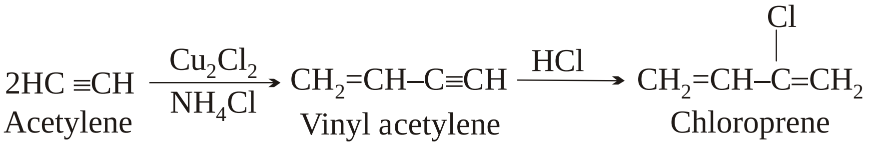
$$CH_2{=}\overset{\overset{G}{|}}{C}{-}CH{=}CH_2$$

where G=H, CH_3 or Cl.

Polymerisation is always carried out in the presence of Zieglar-Natta catalyst which gives stereo regular polymers.

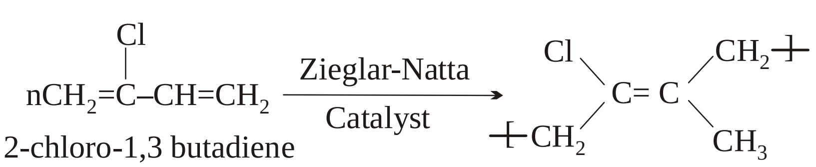


Neoprene was the first synthetic rubber manufactured on large scale. It is also called dieprene. Its monomer, chloroprene(2-chlorobutadiene) is prepared from acetylene.



$$\underset{\text{Acetylene}}{2HC\equiv CH}\xrightarrow[NH_4Cl]{Cu_2Cl_2}\underset{\text{Vinyl acetylene}}{CH_2{=}CH{-}C\equiv CH}\xrightarrow{HCl}\underset{\text{Chloroprene}}{CH_2{=}CH{-}\overset{\overset{Cl}{|}}{C}{=}CH_2}$$

Cloroprene undergoes free radical polymerisation to form neoprene (polychloroprene).



$$nCH_2=\overset{\overset{Cl}{|}}{C}-CH=CH_2 \xrightarrow[\text{Catalyst}]{\text{Zieglar-Natta}} \left[CH_2-C(Cl)=C(CH_3)-CH_2 \right]$$

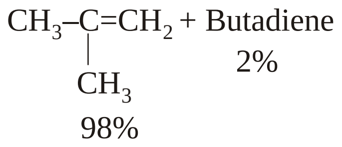
2-chloro-1,3 butadiene
or
chloroprene

(Trans polymer
Trans polychloroprene
or Neoprene

Many of the properties of neoprene are similar to natural rubber but neoprene is more resistant to action of oils, gasoline and other hydrocarbons. It is also resistant to sunlight, oxygen, ozone and heat. It is non - inflammable.It is used for making automobile and refrigerator parts, hoses for petrol and oil containers, insulation of electric wires and conveyor belts.

2. Copolymers

The following synthetic rubbers are example of copolymers.

Synthetic rubber	**Monomers**
1. Buna-S, SBR (Styrene-butadiene rubber)	$C_6H_5-CH=CH_2$ + $CH_2=CH-CH=CH_2$ (25%) (75%)
2. Buna-N, NBR (Nitrile-butadiene rubber)	$CH_2=CH-CN$ + $CH_2=CH-CH=CH_2$ (25%) (75%)
3. Butyl rubber	 $CH_3-\underset{\underset{CH_3}{\vert}}{C}=CH_2$ + Butadiene 98% 2%
4. ABS; Acrylonitrile, Butadiene, Styrene	$CH_2=CH-CN$ + $CH_2=CH-CH=CH_2$ + $C_6H_5CH=CH_2$

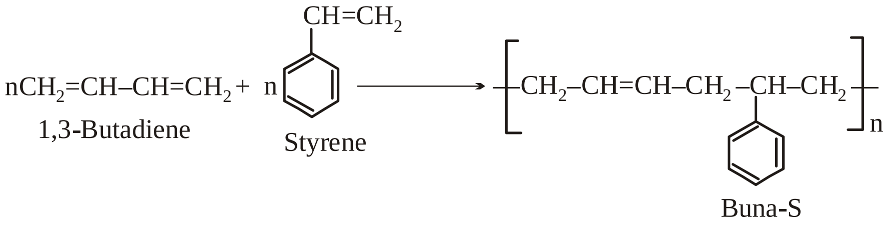
(a) **Thiokol :** Thiokol is made by polymerising ethylene chloride and sodium polysulphide.

$$2Cl-CH_2-CH_2-Cl + Na-S-S-Na \xrightarrow{\text{Polymerisation}} -CH_2-CH_2-S-S-CH_2-CH_2-S-S-CH_2-CH_2-$$

Thiokol rubber

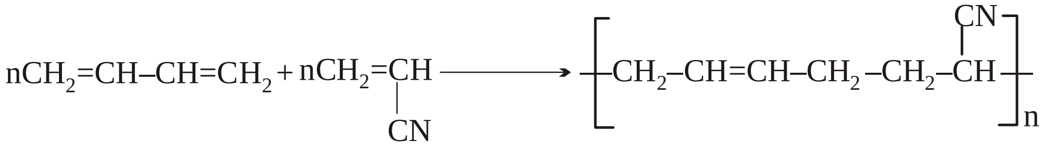
The repeating unit is $-CH_2-S-S-CH_2-$.Thiokol is chemically resistant polymer. It is used in the manufacture of hoses and tank linings, engine gaskets and rocket fuel when mixed with oxidising agents.

(b) **Buna -S (SBR : Styrene-butadiene rubber) :** Buna-S rubber is a copolymer of three moles of butadiene and one mole of styrene. In Buna-S, 'Bu' stands for butadiene, 'na' for symbol of sodium (Na) which is a polymerizing agent and 'S' stands for styrene. It is an elastomer (General purpose styrene Rubber or GRS).



Buna-S is generally compounded with carbon black and vulcanised with sulpur. It is extremely resistant to wear and tear and therefore used in the manufacture of tyres and other mechanical rubber goods. It is obtained as a result of free radical copolymerisation of its monomers.

(c) **Buna-N :** It is obtained by copolymerisation of butadiene and acrylonitirile (General Purpose Rubber acrylonitirle or GRA).



$$nCH_2{=}CH{-}CH{=}CH_2 + nCH_2{=}\underset{\displaystyle CN}{\underset{|}{C}}H \longrightarrow \left[CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\overset{\displaystyle CN}{\overset{|}{C}}H \right]_n$$

It is very rigid and is very resistant to action of petrol, lubricating oil and many organic solvents. It is mainly used for making fuel tanks.

(d) **Cold Rubber :** Cold rubber is obtained by polymerisation of butadiene and styrene at –18° to 5°C temperature in the presence of redox system. Cold rubber has a greater tensile strength and greater resistance ot abrasion than SBR.

NYLON

Nylon is used as a general name for all synthetic fibres forming polyamides, i.e.,having a protein like structure. A number is usually suffixed with the name 'nylon' which refers to the number of carbon atoms present in the monomers.

(1) **NYLON - 66** (Nylon six, six)

It is obtained by the condensation polymerisation of hexamethylenediamine (a diamine with six carbon atoms) and adipic acid (a dibasic acid having 6 carbon atoms).

$$\underset{\text{Adipic acid}}{nHOOC(CH_2)_4COOH} + \underset{\substack{\text{Hexamethylene}\\\text{diamine}}}{nH_2N(CH_2)_6\,NH_2} \xrightarrow[\substack{\text{High pressure}\\-(n-1)\ H_2O}]{280°C} \underset{\text{Nylon - 66}}{\left[OC(CH_2)_4CONH(CH_2)_6NH \right]_n}$$

(2) **NYON-610** (Nylon six, ten)

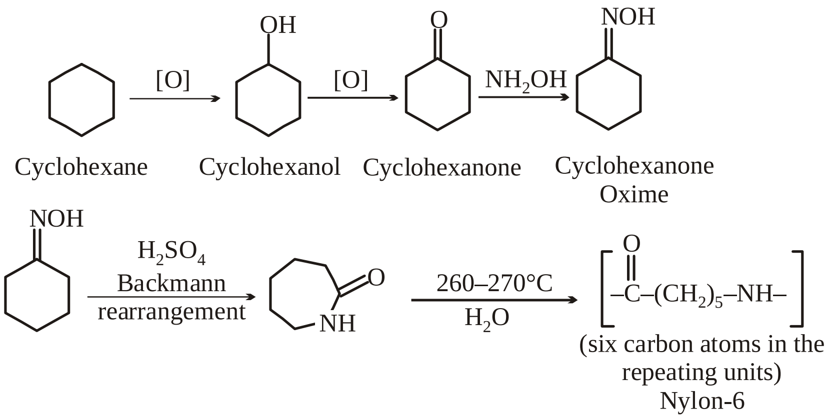
It is obtained by condensation polymerisation of hexamethylenediamine (six carbon atoms) and sebacic acid (a dibasic acid with 10 carbon atoms.)

Nylon fibres are stronger than natural fibres and so are used in making cords and ropes. The fibres are elastic, light, very strong and flexible. They have drip dry property and retain creases. It is inert towards chemicals and biological agents. It can be blended with wool. Nylon fibres are used in making garments, carpets, fabrics, tyre cords, ropes, etc.

(3) **NYON-6 (Perlon L)**

A polyamide closely related to nylon is known as perlon L (Germany) or Nylon - 6 (USA). It is prepared by prolonged heating of caprolactum at 260–270°C. It is formed by self condensation of a large number of molecules of amino caproic acid. Since, caprolactum is more easily available, it is used for polymerization, with is carried out in the presence of H_2O that first hydrolyses the lactam to amino acid. Subsequently, the amino acid can react with the lactam and the process goes on and onto form the polyamide polymer.

Carpolactam is obtained by Backmann rearrangement of cyclohexanone oxime.



(4) NYON-2–NYLON-6

It is in alternating polyamide copolymer of glycine and amino caproic acid and is biodegradable.

POLYETHYLENE

Polyethylene is of two types :

(a) Low Density Poly Ethylene (LDPE) : It is manufactured by heating ethylene at 200°C under a pressure of 1500 atmospheres and in the presence of traces of oxygen. This polymerisation is a free radical polymerisation.

$$nCH_2{=}CH_2 \xrightarrow[1500\text{ atm.}]{200°C} \left[CH_2{-}CH_2 \right]_n$$

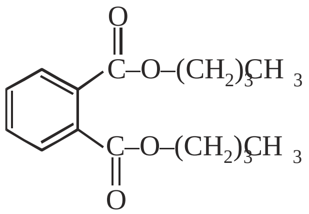
The polyethylene produced has a molecular mass of about 20,000 and has a branched structure. Due to this, polyethylene has a low density (0.92) and low melting point(110°C). That is why polyethylene prepared by free radical polymerisation is called low density polyethylene. It is a transparent polymer of moderate tensile strength and high toughness. It is widely used as a packing material and as insulation for electrical wires and cables.

(b) High Density Poly Ethylene (HDPE) : It is prepared by the use of Zieglar - Natta catalyst at 160°C under pressure of 6 to 7 atmosphere.

The polymer is linear chain, hence it has high density (0.97) and has high melting point (130°C). That is why it is called high density polyethylene. It is a translucent polymer. It has greater toughness, hardness and tensile strength than low density polyethylene. It is used in the manufacture of containers (buckets, tubes), house wares, bottles and toys.

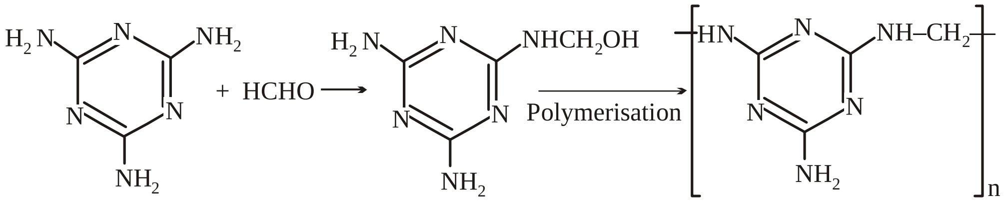
PLASTICISER

A plasticiser is an organic compound that dissolves in the polymer and allows the polymer chains to slide past one another. This makes polymer more flexible. Dibutylphthalate is a commonly used plasticiser.



MELAMINE - FORMALDEHYDE RESIN

This resin is formed by condensation polymerisation of melamine and formaldehyde.



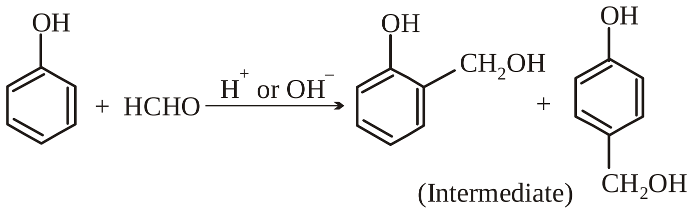
(Intermediate)

Melamine-formaldehyde polymer

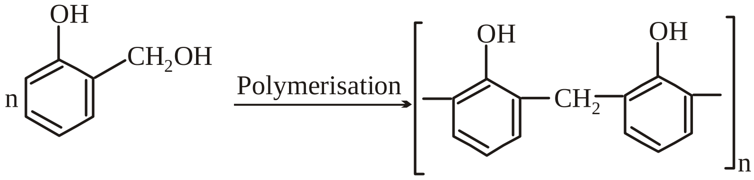
It is a quite hard polymer and is used widely for making plastic crockery under the name melamine.The articles made from this polymer do not break even when dropped from considerable height.

BAKELITE

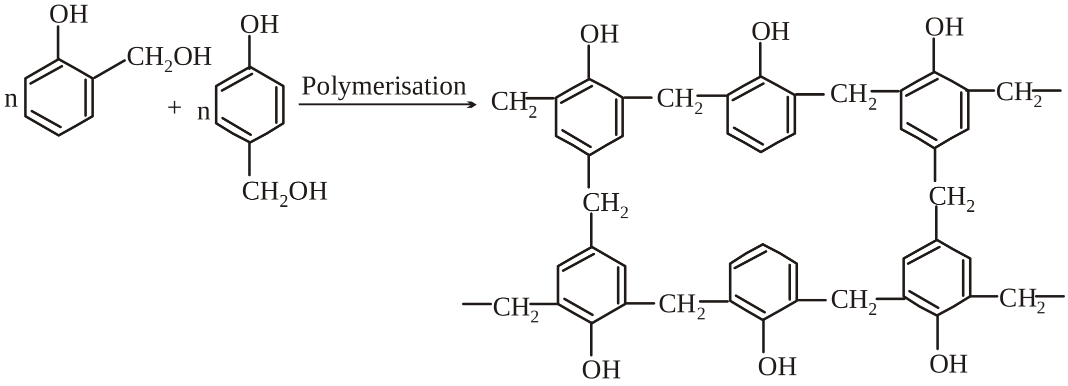
Phenol-formaldehyde resins are obtained by the reaction of phenol and formaldehyde in the presence of either an acid or a basic catalyst. The reaction starts with the initial formation of ortho and para-hydroxymethyl phenol derivatives, which further react with phenol to form compounds where rings are joined to each other with $–CH_2$ groups. The reaction involves the formation of methylene bridges in ortho, para or both ortho and para positions. Linear or cross - linked materials are obtained depending on the conditions of the reaction.



(Intermediate)
o-and p-hydroxymethyl phenol



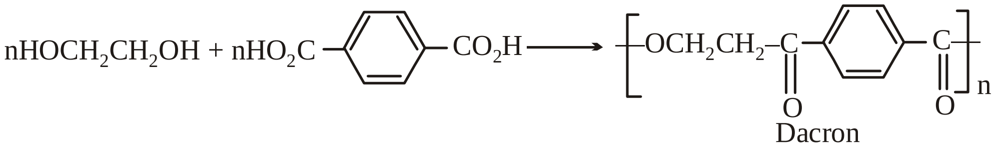
Linear polymer
Novolac



Cross - linked polymer (Bakelite)

POLYESTERS

Dacron is a common polyester, prepared using ethylene glycol and terephthalic acid. The reaction is carried out at 140° to 180° C in the presence of zinc acetate and Sb_2O_3 as catalyst.



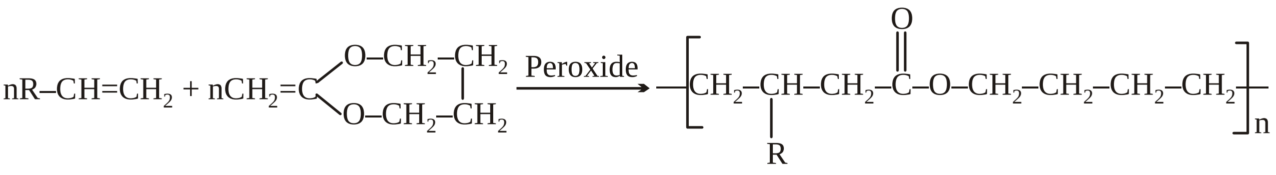
The terylene fibre (Dacron) is crease resistant and has low moisture absorption. It has high tensile strength. It is mainly used in making wash and wear garments, in blending with wood to provide better crease and wrinkle resistance.

BIODEGRADABLE POLYMERS

By far the largest use of synthetic polymers is as plastic. A major portion of it is used as throwaway containers and packing materials. Since plastics do not disintegrate by themselves, they are not biodegradable over a period of time. Non - biodegradability is due the carbon-carbon bonds of addition polymers which are inert to enzyme catalysed reaction. These polymers create pollution problem.

Biodegradable polymers are the polymers that can be broken into small segments by enzyme catalysed reactions using enzymes produced by microorganisms. In biodegradable polymers, bonds that can be broken by the enzymes are inserted into the polymers. Therefore, when they are buried as waste, enzymes present in the ground can degrade the polymer.

One method involves inserting hydrolysable ester group into the polymer. For example, when acetal (I) is added during the polymerization of alkene, ester group is inserted into the polymeric chains.



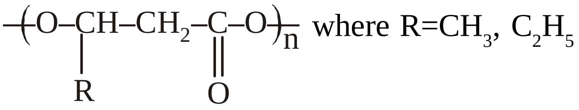
Ester linkage attacked by enzyme

Aliphatic polyesters are important class of biodegradable polymers. some examples are described below:

(1) Poly - Hydroxybutyrate-CO-β-Hydroxyvalerate (PHBV)

It is a copolymer of 3 - hydroxybutanoic acid and 3 hydroxypentanoic acid, in which the monomer units are connected by ester linkages.

$CH_3–CH(OH)–CH_2–COOH + CH_3 –CH_2–CH(OH)–CH_2–COOH \rightarrow$



$$\left(O–\underset{R}{CH}–CH_2–\underset{O}{\underset{\|}{C}}–O \right)_n \text{ where } R=CH_3,\ C_2H_5$$

The properties of PHBV vary according to the ratio of both the acids. 3-Hydroxybutanoic acid provides stiffness and 3-hydroxypentanoic acid imparts flexibility to the co-polymer. It is used in specialty packaging, orthopaedic devices and even in controlled drug relase. When a drug is put in a capsule of PHBV, It is released only after the polymer is degraded. PHBV also undergoes bacterial degradation in the environment.

(2) POLY (GLYCOLIC ACID) AND POLY (LACTIC ACID)

They constitute commercially successful biodegradable polymers such as sutures. Dextron was the first bioadsorbable suture made for biodegradable polyesters for post - operative stitches.

MOLECULAR MASS OF POLYMER

Normally, a polymer contains chains of varying lengths and therefore, its molecular mass is always expressed as an average. In contrast, natural polymers such as protein contains chain of identical length and hence, have definite molecular mass.

The molecular mass of a polymer is expressed as

(a) Number average molecular mass $(\overline{M}_n)$

$$\overline{M}_n = \frac{\sum N_i M_i}{\sum_i N_i}$$

where N_i is the number of molecules of molecular mass M_i

(b) Weight average molecular mass $(\overline{M}_w)$

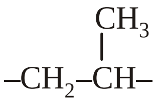
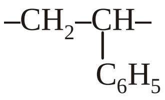
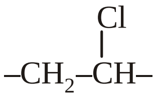
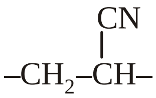
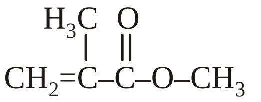
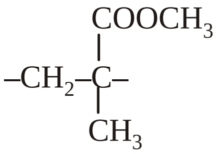
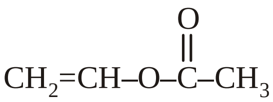
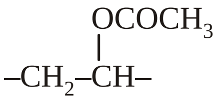
$$\overline{M}_w = \frac{\sum N_i M_i^2}{\sum_i N_i M_i}$$

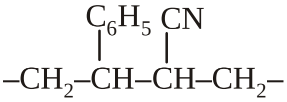
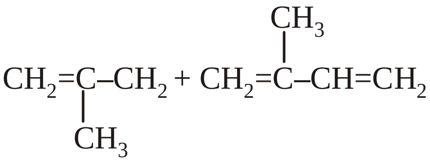
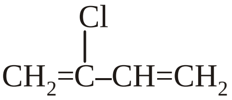
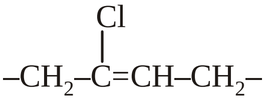
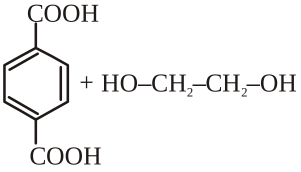
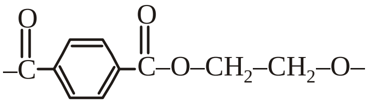
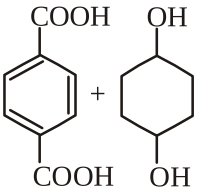
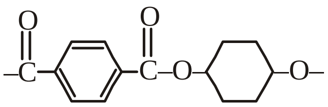
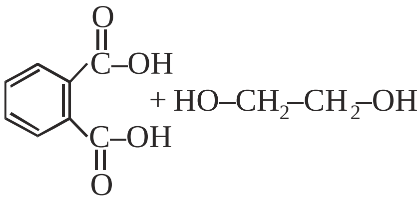
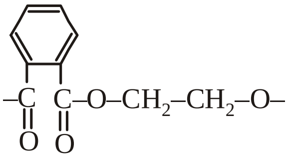
where N_i is the number of molecules of molecular mass M_i. Methods such as light scattering and ultracentrifuge depend on the mass of the individual molecules and yield weight average molecular masses. $\overline{M}_n$ is determined by employing methods which depend upon the number of molecules present in the polymer sample viz. colligative properties like osmotic pressure.

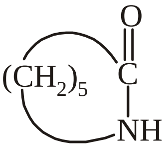
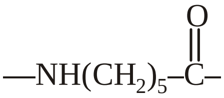
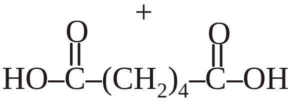
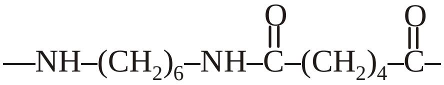
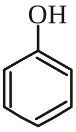
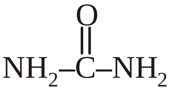
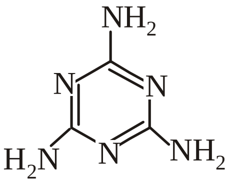
The ratio of the weight and number average molecular masses ($\overline{M}_w / \overline{M}_n$) is called Poly Dispersity Index (PDI). Some natural polymers, which are generally monodisperesed, the PDI is unity (i.e. $\overline{M}_w = \overline{M}_n$).

In synthetic polymers, which are always polydispersed, PDI > 1 because $\overline{M}_w$ is always higher than $\overline{M}_n$.

COMMON POLYMERS

Monomer	Repeatng unit	Polymer
1. $CH_2=CH_2$ Ethylene	$-CH_2-CH_2-$	Polyethylene
2. $CH_3-CH=CH_2$ Propene	 $-CH_2-\overset{\overset{CH_3}{\vert}}{CH}-$	Polypropene
3. $C_6H_5-CH=CH_2$ Styrene	 $-CH_2-\underset{\underset{C_6H_5}{\vert}}{CH}-$	Polystyrene
4. $CF_2=CF_2$ Tetrafluoroethylene	$-CF_2-CF_2-$	Polytetrafluoroethylene (PTFE), Teflon
5. $CH_2=CH-Cl$ Vinyl chloride	 $-CH_2-\overset{\overset{Cl}{\vert}}{CH}-$	Polyvinyl Chloride(PVC)
6. $CH_2=CH-CN$ Vinyl cyanide or Acrylonitrile	 $-CH_2-\overset{\overset{CN}{\vert}}{CH}-$	Polyvinyl cyanide, poly acrylonitrile, Orlon.
7.  $CH_2=\overset{\overset{H_3C}{\vert}}{C}-\overset{\overset{O}{\Vert}}{C}-O-CH_3$ Methyl methacrylate	 $-CH_2-\overset{\overset{COOCH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-$	Polymethyl metha acrylate, Plexiglas, Lucite
8.  $CH_2=CH-O-\overset{\overset{O}{\Vert}}{C}-CH_3$ Vinyl acetate	 $-CH_2-\overset{\overset{OCOCH_3}{\vert}}{CH}-$	Polyvinyl Acetate
9. $CH_2=CH-CH=CH_2$ 1,3-butadiene	$-CH_2-CH=CH-CH_2-$	Polybutadiene, Buna rubber
10. $CH_2=CH-Cl$ (vinyl chloride) + $CH_2=CCl_2$ (Vinylidene chloride)	 $-CH_2-\overset{\overset{Cl}{\vert}}{CH}-CCl_2-CH_2-$	Saran

11. $C_6H_5-CH=CH_2$ (Styrene) + $CH_2=CH-CN$ (acrylonitrile)	 $-CH_2-CH(C_6H_5)-CH(CN)-CH_2-$	SAN
12. $CH_2=CH-CN + CH_2=CH-CH=CH_2$ + $C_6H_5-CH=CH_2$	—	ABS
13.  $CH_2=C(CH_3)-CH_3 + CH_2=C(CH_3)-CH=CH_2$	—	Butyl rubber
14. $C_6H_5-CH=CH_2+CH_2=CH-CH=CH_2$	—	Buna -S, SBR
15. $CH_2=CH-CN + C_6H_5-CH=CH_2$	—	Buna-N, NBR
16.  $CH_2=C(Cl)-CH=CH_2$ Cloroprene	 $-CH_2-C(Cl)=CH-CH_2-$	Neoprene
17. 		Poly(ethylene terephthalate, Terylene, Dacron or Mylar
18. 		Kodel Polyster
19. 		Polyethylene phthatate alkyd resin (Glyptal)

20.  Caprolactam	 $—NH(CH_2)_5–\overset{\overset{O}{\parallel}}{C}–$	Nylon-6
21. $NH_2(CH_2)_6–NH_2$ Hexamethylenediamine +  $HO–\overset{\overset{O}{\parallel}}{C}–(CH_2)_4–\overset{\overset{O}{\parallel}}{C}–OH$ Adipic Acid	 $—NH–(CH_2)_6–NH–\overset{\overset{O}{\parallel}}{C}–(CH_2)_4–\overset{\overset{O}{\parallel}}{C}–$	Nylon - 66
22.  + HCHO	—	Bakelite or resol
23.  $NH_2–\overset{\overset{O}{\parallel}}{C}–NH_2$ + HCHO	—	Urea- formaldehyde resin
24.  + HCHO Melamine	—	Malamine formaldehyde resin

CHEMICAL TESTS FOR FUNCTIONAL GROUPS

- Elemental analysis, physical, spectral and solubility test give a reasonable idea regarding the identity of unknown compound.
- Despite the tremendous importance and ease of spectral analysis, chemical tests are indispensable to complete characterization.

1. Test For Alcohols :

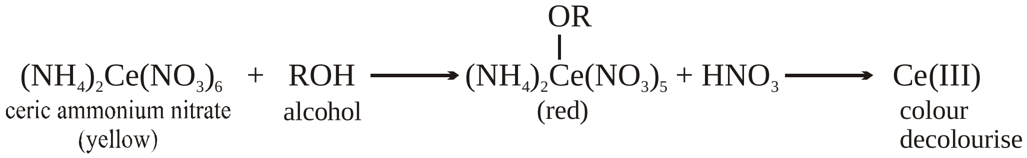
(i) Sodium Metal

$$\underset{\text{Alcohol}}{ROH} + Na \longrightarrow \underset{\text{(Sodium alkoxide)}}{RO^{-}Na^{+}} + \frac{1}{2}H_2(g)$$

- When Na-metal reated with alcohol H_2(g) evolve
- It accure in 1°, 2° & 3°
- The rate is highly variable and depends upon the alcohol structure.
- Other Functional groups that evolve $H_2(\uparrow)$

R_2NH, RSH, $RC\equiv C\text{-}H$, RCO_2H etc.

(ii) Ceric Ammonium Nitrate Oxidation (CAN Test)

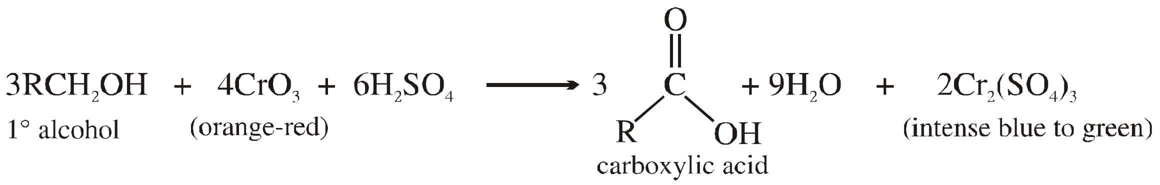


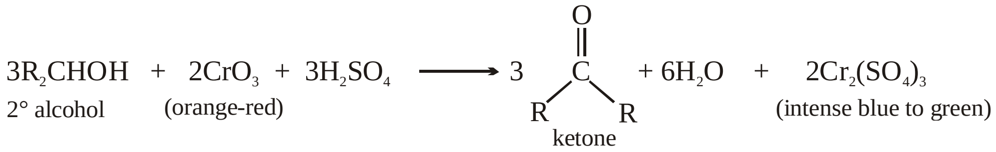
$$\underset{\substack{\text{ceric ammonium nitrate}\\ \text{(yellow)}}}{(NH_4)_2Ce(NO_3)_6} + \underset{\text{alcohol}}{ROH} \longrightarrow \underset{\text{(red)}}{(NH_4)_2\overset{OR}{\overset{|}{Ce}}(NO_3)_5} + HNO_3 \longrightarrow \underset{\substack{\text{colour}\\ \text{decolourise}}}{Ce(III)}$$

- **<u>Positive Test</u>**: Color changes from yellow to red first then to colorless solution. (1 min. to 12 hrs)
- A positive test includes successively the formation, and then the disappearance of the red color.
- Very good test for 1°, 2° alcohol, but slow for 3° alcohol
- **<u>Note</u>**: Phenols gives brown or black colour.

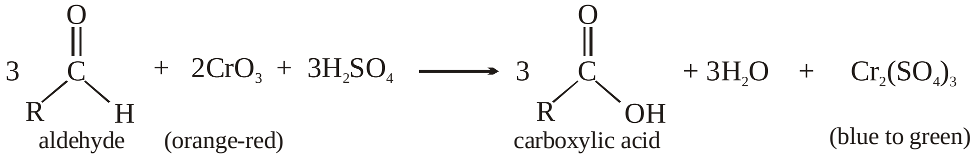
(iii) Jones Oxidation: Chromic anhydride or Chromium Trioxide (CrO_3)

- A positive test for 1°, and 2° alcohols consists in the changes from an orange-red color (Cr^{6+}) to opaque suspension with green to blue color (Cr^{+3}) in 2 sec.
- 3° alcohols give no visible reaction within 2 sec. remaining orange
- **<u>Note</u>**: Aldehydes give positive result.





$$\underset{\text{2° alcohol}}{3R_2CHOH} + \underset{\text{(orange-red)}}{2CrO_3} + 3H_2SO_4 \longrightarrow 3\underset{\text{ketone}}{R_2C{=}O} + 6H_2O + \underset{\text{(intense blue to green)}}{2Cr_2(SO_4)_3}$$



$$3\underset{\text{aldehyde}}{RCHO} + \underset{\text{(orange-red)}}{2CrO_3} + 3H_2SO_4 \longrightarrow 3\underset{\text{carboxylic acid}}{RCOOH} + 3H_2O + \underset{\text{(blue to green)}}{Cr_2(SO_4)_3}$$

(iv) Lucas Test

- This test distinguishes 1°, 2° & 3° alcohol from each other
- It uses, anhydrous $ZnCl_2$ in conc. HCl (lucas reagent)

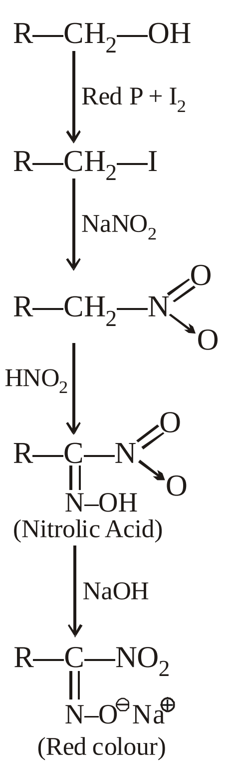
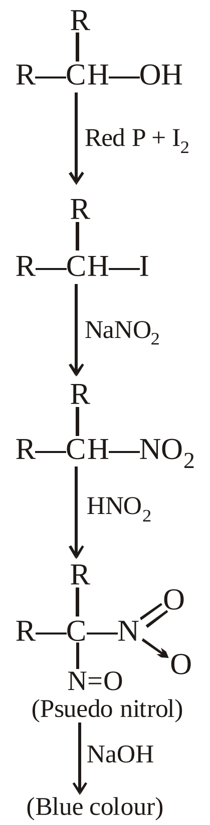
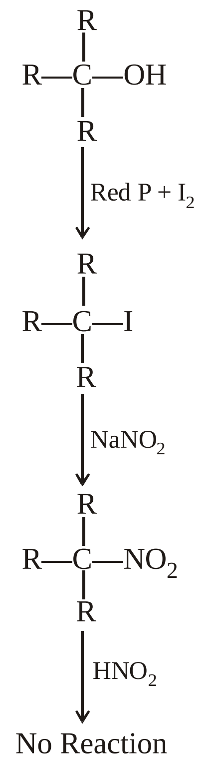
$$R{-}OH \xrightarrow{(HCl + ZnCl_2)} R{-}Cl + H_2O$$

- 3° alcohols give white turbidity solution immediately
- 2° alcohols give white turbidity solution within 5 to 10 minutes
- 1° alcohols does not give white turbidity at room temperature

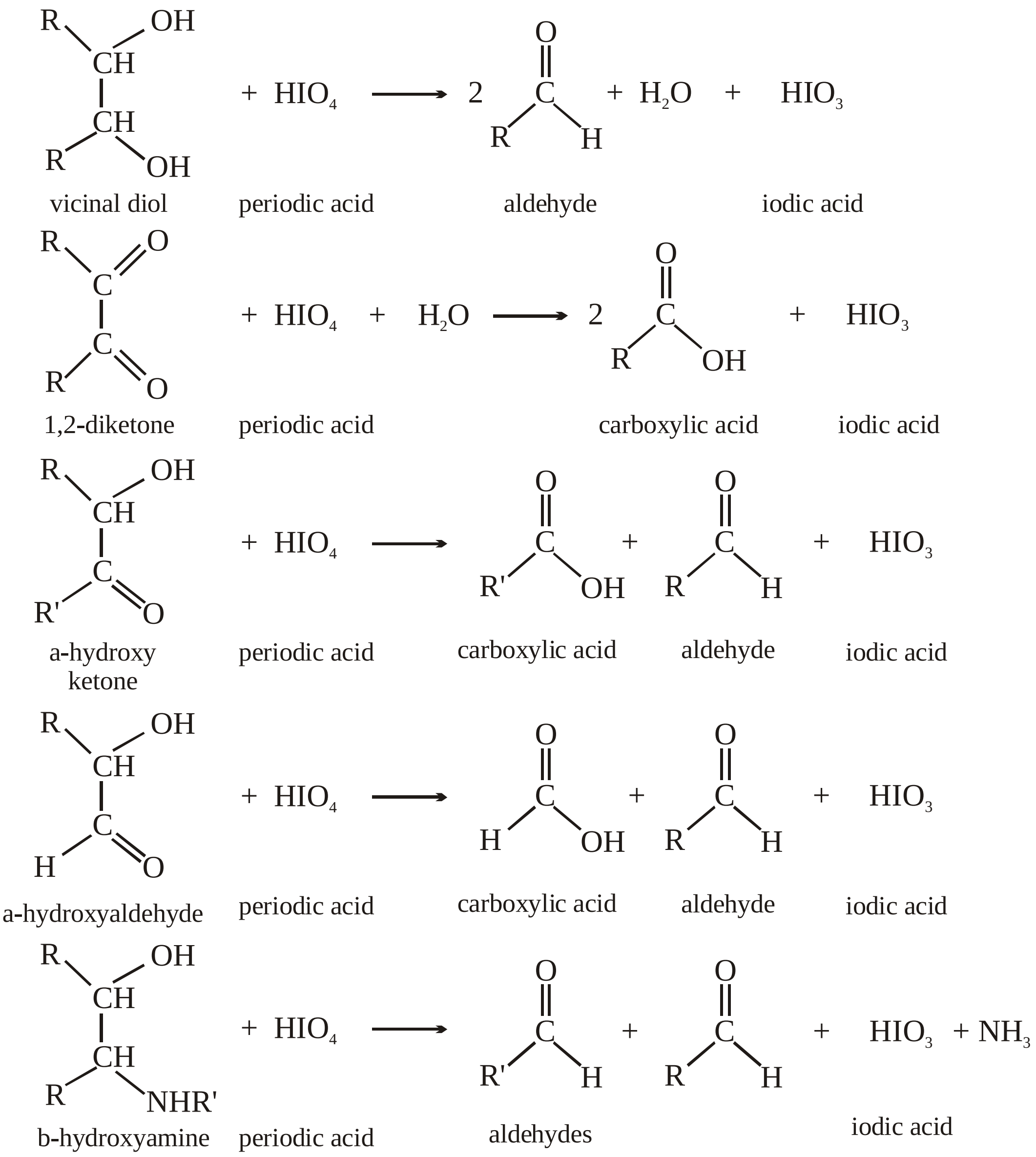
Note : Benzyl alcohol also react immediately

(v) Victor-Mayer Test

- This test also distinguishes 1°, 2° & 3° alcohol

1° - Alcohol	2° - Alcohol	3° - Alcohol
 $R{-}CH_2{-}OH \xrightarrow{\text{Red P} + I_2} R{-}CH_2{-}I \xrightarrow{NaNO_2} R{-}CH_2{-}NO_2 \xrightarrow{HNO_2} \underset{\text{(Nitrolic Acid)}}{R{-}C({=}N{-}OH){-}NO_2} \xrightarrow{NaOH} \underset{\text{(Red colour)}}{R{-}C({=}N{-}O^{\ominus}Na^{\oplus}){-}NO_2}$	 $R{-}\overset{R}{CH}{-}OH \xrightarrow{\text{Red P} + I_2} R{-}\overset{R}{CH}{-}I \xrightarrow{NaNO_2} R{-}\overset{R}{CH}{-}NO_2 \xrightarrow{HNO_2} \underset{\text{(Psuedo nitrol)}}{R{-}\overset{R}{\underset{N=O}{C}}{-}NO_2} \xrightarrow{NaOH} \text{(Blue colour)}$	 $R{-}\overset{R}{\underset{R}{C}}{-}OH \xrightarrow{\text{Red P} + I_2} R{-}\overset{R}{\underset{R}{C}}{-}I \xrightarrow{NaNO_2} R{-}\overset{R}{\underset{R}{C}}{-}NO_2 \xrightarrow{HNO_2} \text{No Reaction}$

(vi) Periodic Acid (HIO_4) Test for detection of Vicinal Diols and Related Compounds



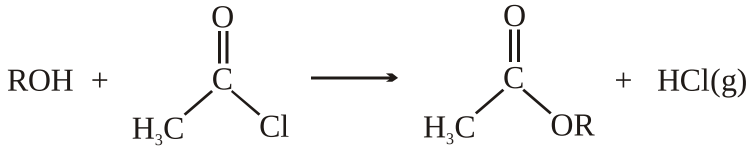
- The iodic acid is detected with 5% $AgNO_3$ solution -an immediate precipitation of silver iodate occurs.

$$\underset{\text{Iodic acid}}{HIO_3} + \underset{\text{Silver nitrate}}{AgNO_3} \longrightarrow HNO_3 + \underset{\text{Silver iodate (white)}}{AgIO_3(s)}$$

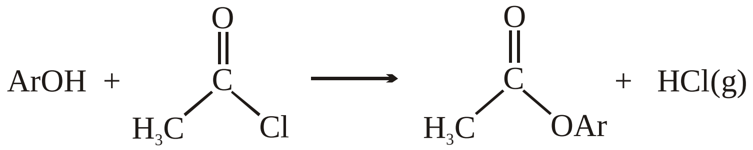
- Olefins, 2° alcohols, 1,3-glycols, ketones and aldehydes are not affected by HIO_4 under the test condition.

(vii) Acetyl Chloride

- Positive Test: Evolution of HCl gas and formation of ester as a top layer

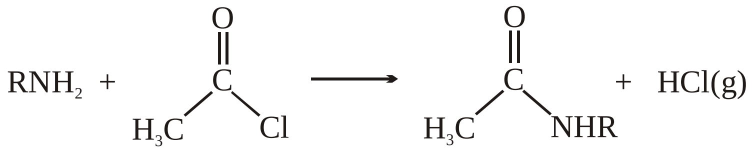


alcohol acetyl chloride ester

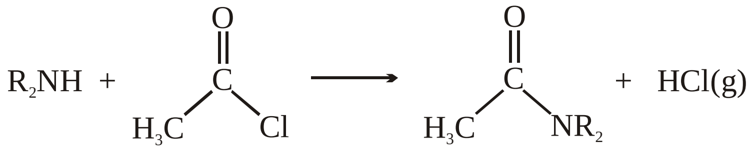


phenol acetyl chloride ester

- 3° alcohols form primarily alkyl chloride due to the reaction of the liberated HCl on another molecule of the alcohol.
- Other functional groups that give positive test: 1° and 2° amines



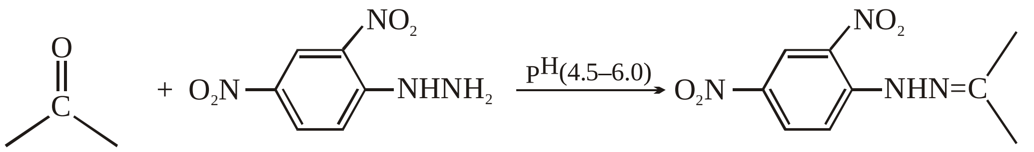
1°amine acetyl chloride amide



2°amine acetyl chloride amide

2. Classification Tests For Aldehydes and Ketone

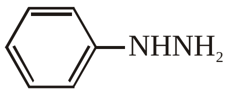
(i) 2,4-Dinitrophenyl Hydrazine



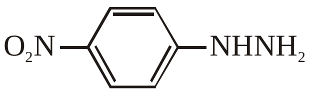
aldehyde or ketone 2,4-dinitrophenylhydrazine 2,4-dinitrophenylhydrazone

- **Positive Test**: formation of yellow, orange or red ppt.
- The precipitate may be oily at first and become crystalline on standing.

(ii) Phenyl hydrazine and p-Nitrophenyl hydrazine.



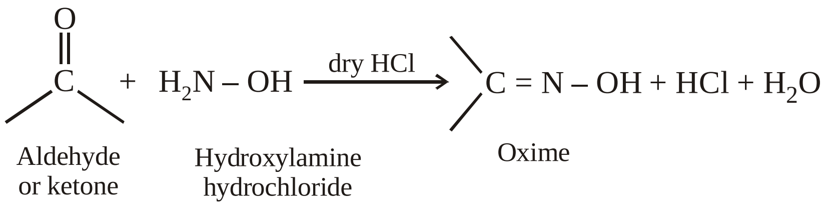
phenylhydrazine



p-nitrophenylhydrazine

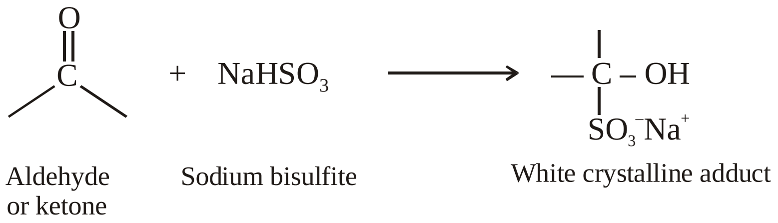
Positive Test: formation of yellow ppt.

(iii) Hydroxylamine Hydrochloride



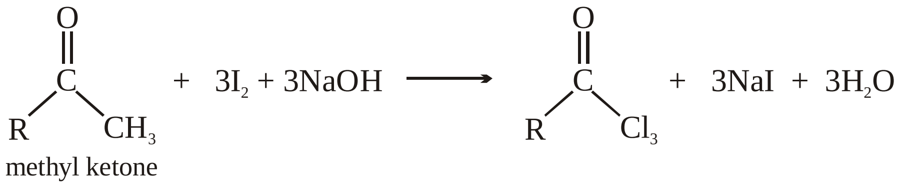
The liberation of hydrogen chloride can be detected by the change in colour from orange to red of a pH indicator.

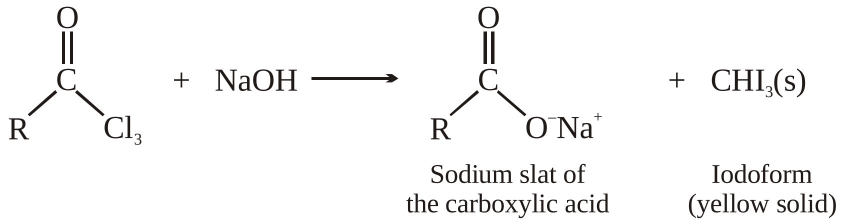
(iv) Sodium Bisulfite ($NaHSO_3$)



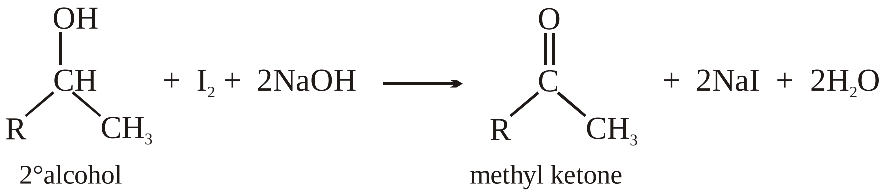
- **<u>Positive Test:</u>** By aldehydes and methyl ketone
- Only some cyclic ketones give positive results (ppt)
- This reaction is greatly inhibited by the steric constraints about the carbonyl group.

(v) Iodoform Test (For Methyl Ketones)

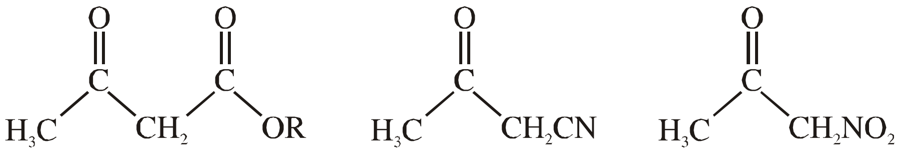




- **<u>Positive Test:</u>** Yellow ppt for methyl ketones
- **<u>Disadvantages</u>**: Some compounds that can be easily oxidized to methyl ketones give also positive results
- The principal types of compounds that give a positive test:



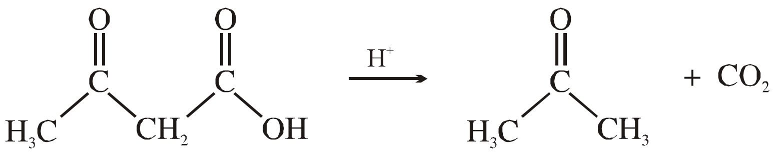
- **The test is negative for the following type:**

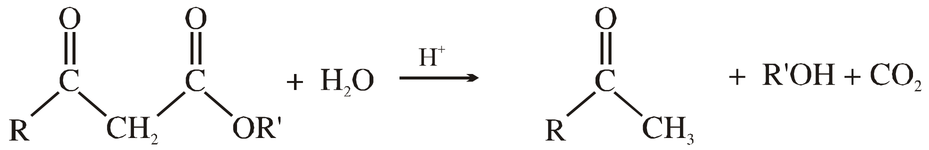


etc...,

In such compounds the reagent removes the acetyl group and converts it to acetic acid, which resists iodination.

Acetoacetic acid is unstable, acidic aqueous solutions decompose to give CO_2 and acetone.





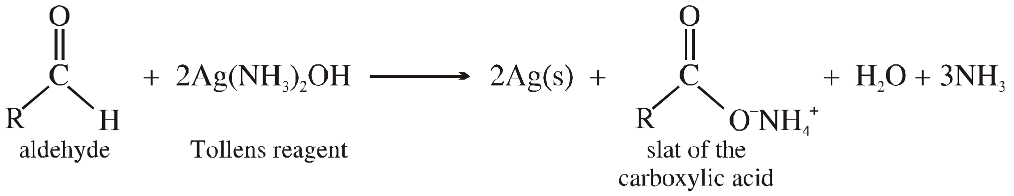
give positive iodoform test

3. Tests that give positive results with aldehydes and negative results with Ketones

(i) Jones Oxidation: Chromic anhydride or Chromium Trioxide (CrO_3)

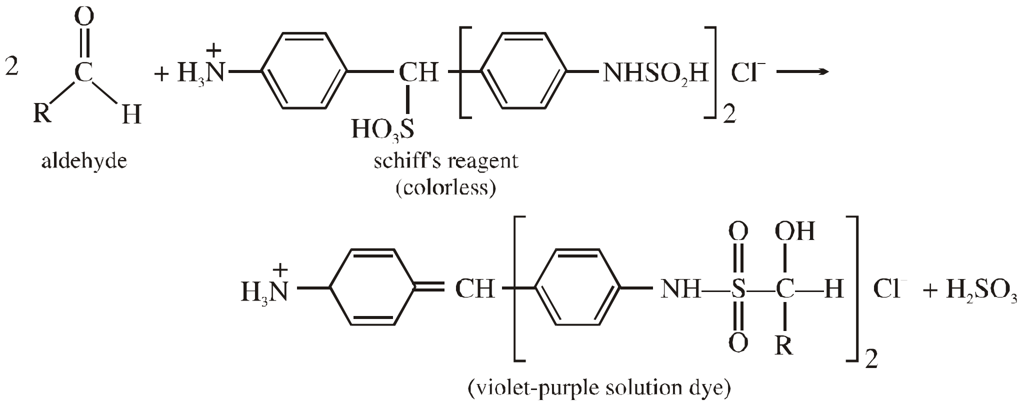
(Refer Jones Oxidation for alcohols at Page No. 22)

(ii) Tollens Reagents $Ag(NH_3)_2OH$



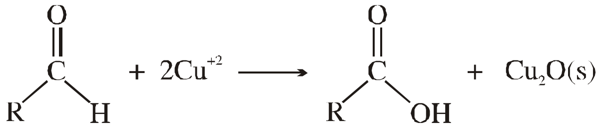
- **Positive Test:** Formation of silver mirror (Ag) or colloidal (granular) gray or black Ag precipitate.

(iii) Schiff's Reagent

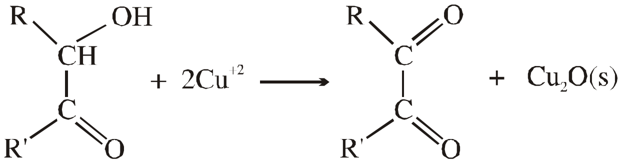


(iv) Bendicts solution and Fehling's Solution

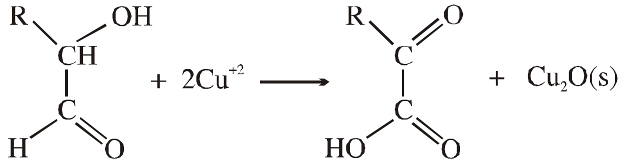
- **Positive Test**: yellow or yellowish green ppt.
- All aldehydes give positive result except aromatic aldehydes (negative)



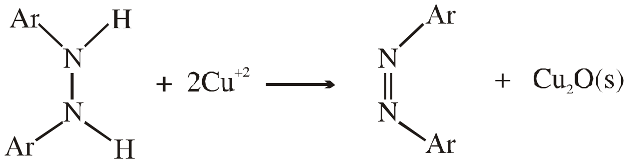
aldehyde (blue) carboxylic acid (red, yellow, or yellowish green)



α-hydroxyketone (blue) 1,2-diketone (red, yellow, or yellowish green)



α-hydroxyaldehyde (blue) 1,2-diketone (red, yellow, or yellowish green)



hydrazobenaene (blue) azocompound (red, yellow, or yellowish green)

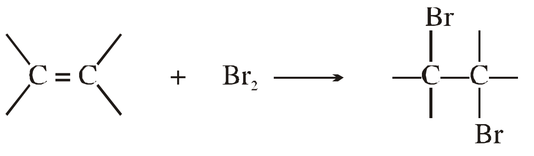
$$ArNHNH_2 + 2Cu^{+2} \longrightarrow ArH + ArOH + N_2(g) + Cu_2O(s)$$

arylhydrazine (blue) phenol (red, yellow, or yellowish green)

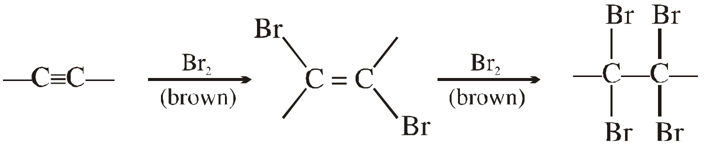
4. Classification Tests for Unsaturation "alkenes & alkynes"

- Alkanes are not usually characterized chemically because they are quite inert to most classification reactions

(i) Bromine in CCl_4



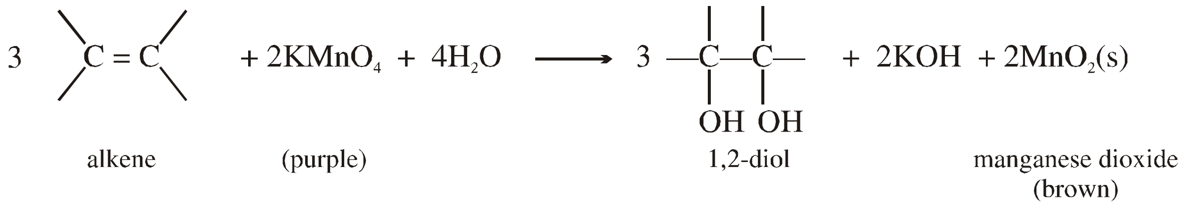
alkene (red-brown) 1,2-dibromoalkane (colourless)

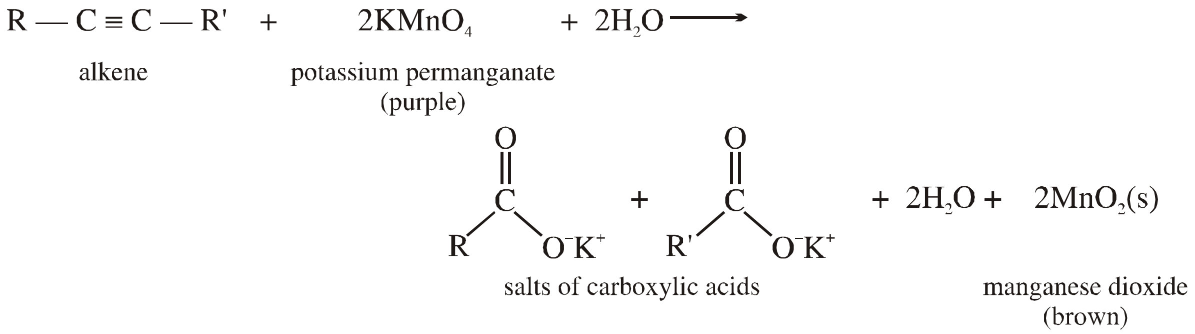


alkene 1,2-dibromoalkane (colourless) 1,1,2,2-tetrabromoalkane (colourless)

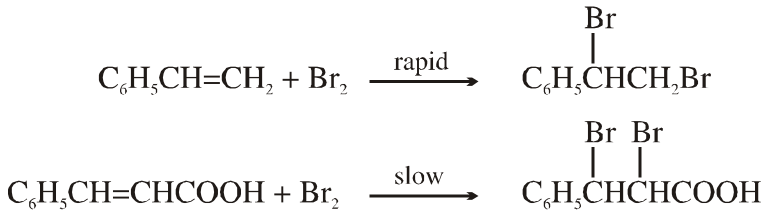
- **Positive Test**: Bromine color discharged without evolution of gas (HBr)
- Alkenes & alkynes give positive results
- If HBr is evolved, it indicates phenols, enols & enolizable compounds ,-,
- Bromine color is discharged by amines to produce a salt, which could be mistaken for addition.

(ii) Baeyer Test ($KMnO_4$ **aqueous)**





- **Positive Test:** Purple color discharges, and brown color ppt (MnO_2) appears
- **Note :** Aldehydes and alcohols also give positive result
- Since the ionic characters of the Br_2 and $KMnO_4$ reactions are very different, there is some complementary character between the two tests.
- For example, some alkenes bearing electron-withdrawing groups undergo rapid reaction with $KMnO_4$ but often slow or negligible reaction with Br_2.



$$C_6H_5CH{=}CH_2 + Br_2 \xrightarrow{\text{rapid}} C_6H_5\overset{\overset{Br}{|}}{C}HCH_2Br$$

$$C_6H_5CH{=}CHCOOH + Br_2 \xrightarrow{\text{slow}} C_6H_5\overset{\overset{Br}{|}}{C}H\overset{\overset{Br}{|}}{C}HCOOH$$

- A few tetrasubstituted olefins such as $C_6H_5CBr{=}CBrC_6H_5$ and $(C_6H_5)_2C{=}C(C_6H_5)_2$ fail to give positive tests with Br_2 in CCl_4 or $KMnO_4$ solution.

5. Tests for Alkyl Halides

- Aliphatic halides are often detected initially by qualitative by halogen analysis **halogen analysis.**

(i) Ethanolic Silver Nitrate & (ii) Sodium Iodide in Acetone

- Both tests involve displacement of halogen:
- $AgNO_3$/ethanol test proceeds by a carbocation (S_N1) process & NaI / acetone test proceeds by a direct displacement (S_N2)

$AgNO_3$/ethanol test : $R_3CX > R_2CHX > RCH_2X$
NaI/acetone test: $R_3CX < R_2CHX < RCH_2X$

(i) Ethanolic Silver Nitrate Solution

- The reaction of alkyl halide with silver nitrate yields a silver halide precipitate

$$\underset{\text{alkyl halide}}{RX} + \underset{\text{silver nitrate}}{AgNO_3} \xrightarrow{CH_3CH_2OH} \underset{\text{silver halide}}{AgX(s)} + RONO_2$$

- **<u>Positive Test</u>**: formation of ppt. indicates 2° and 3° RX
- 1° RX , Ar-X, and vinyl halides give negative Result.
- **<u>Note</u>**: allylic and benzylic RX give positive result
- The identity of the halogen can sometimes be determined from the color of the silver halide: AgCl (white); AgBr (pale yellow); AgI (yellow)

(ii) Sodium Iodide in Acetone Test

- The NaI test can be used to test for the presence of bromine or chlorine.
- Sodium halide (NaX) precipitates from the solution.

$$\underset{\text{Alkyl chloride}}{RCl} + \underset{\text{Sodium iodide}}{NaI} \xrightarrow{\text{Acetone}} \underset{\text{Alkyl iodide}}{RI} + \underset{\text{Sodium chloride}}{NaCl(s)}$$

$$\underset{\text{Alkyl bromide}}{RBr} + \underset{\text{Sodium iodide}}{NaI} \xrightarrow{\text{Acetone}} \underset{\text{Alkyl iodide}}{RI} + \underset{\text{Sodium bromide}}{NaBr(s)}$$

- **<u>Positive Test</u>**: precipitate forms
- Indications : 1º, 2º RX, allylic and benzylic halides. Not good for ArX, vinyl halides ,$HCCl_3$, and 3° RX.
- Since reactivity toward alcoholic silver nitrate is often very different from reactivity toward sodium iodide in acetone, both tests should be used with any halogen compound.

6. Tests for Amines and Amine Salts

(i) Diethyl oxalate test :

- This method helps in the separation of primary, secondary and tertiary amines.
- Primary amines on reaction with diethyl oxalate gives solid oxamide, secondary amine gives liquid oxamic ester and tertiary amine remains unreacted in gaseous form.

$$2RNH_2 + (CO_2Et)_2 \longrightarrow (CONHR)_2 + 2EtOH$$

1. The gaseous tertiary amine is separated out.
2. The solid oxamide is filtered out of the liquid oxamic ester.
3. These products are added to the alkaline solution of NaOH.

In this way, Primary, secondary and tertiary amines are separated by Hoffmann's Method

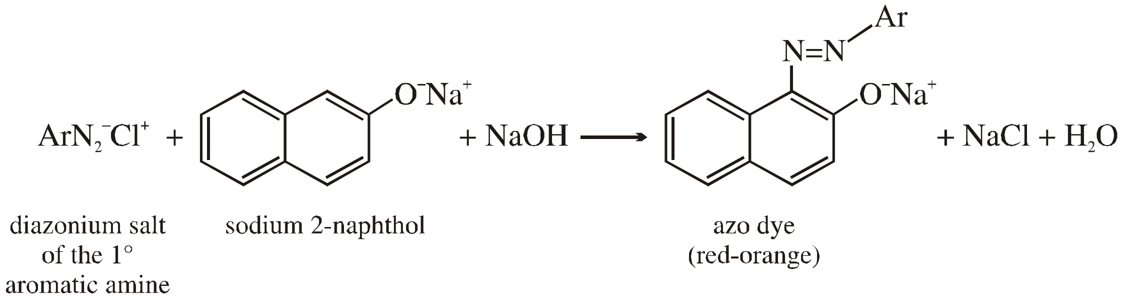
(ii) Nitrous Acid

- Reaction of amines with nitrous acid (HONO) classifies the amine not only as 1°, 2°, or 3°, but also as aliphatic or aromatic.

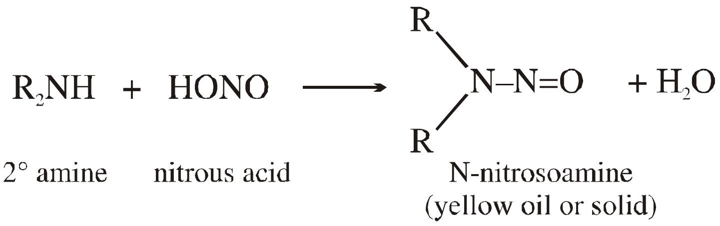
$$\underset{\substack{\text{1°aliphatic}\\\text{amine}}}{RNH_2} + \underset{\substack{\text{nitrous}\\\text{acid}}}{HONO} + 2HCl \longrightarrow \underset{\substack{\text{diazonium salt}\\\text{(unstable at 0°)}}}{[RN_2^+Cl^-]} \xrightarrow[\text{spontaneous}]{H_2O} N_2(g) + ROH + RCl + ROR + \text{alkene}$$

$$\underset{\substack{\text{1°aromatic}\\\text{amine}}}{ArNH_2} + \underset{\substack{\text{nitrous}\\\text{acid}}}{HONO} + HCl \longrightarrow \underset{\substack{\text{diazonium salt}\\\text{(unstable at 0°)}}}{ArN_2^+Cl^-} \xrightarrow{H_2O} N_2(g) + ArOH + HCl$$

- The diazonium salt of the primary aromatic amine reacts with sodium 2-napthol to produce a red-orange azo dye.



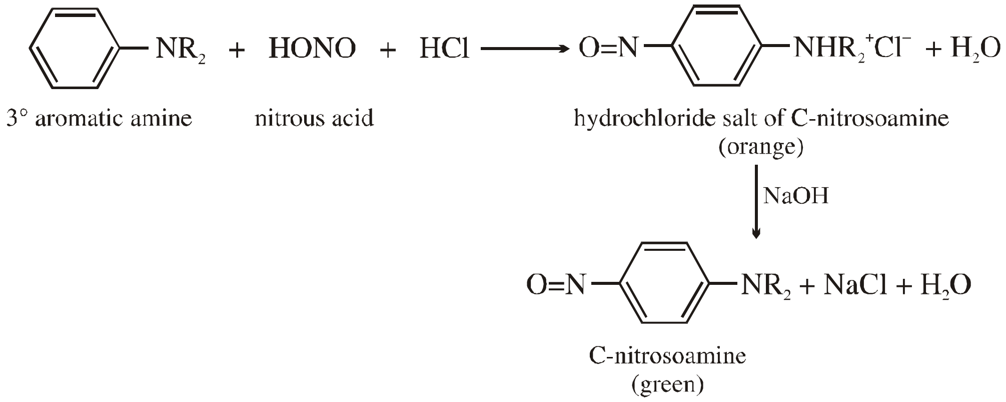
- 2° amines undergo a reaction with nitrous acid to form N-nitrosoamine, which are usually yellow solids.



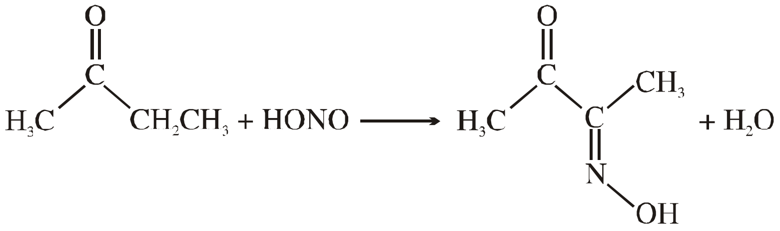
- 3° aliphatic amines do not react with nitrous acid, but they form a soluble salt. The reaction mixture gives an immediate positive test on the starch-iodide paper for nitrous acid.

$$\underset{\text{3° aliphatic amine}}{R_3N} + H^+ \longrightarrow \underset{\text{(soluble)}}{R_3NH^+}$$

- 3° aromatic amines react with nitrous acid to form the orange-colored hydrochloride salt of the C-nitrosoamine. Treating the solution with base liberates the blue or green C-nitrosoamine.



- Although nitrous acid is useful for characterizing amines, other functional groups also react.
- A methylene group adjacent to a keto group is converted to an oximino group and alkyl mercaptans yield red S-alkyl thionitrites.



$$RCH_2SH + HONO \longrightarrow \underset{\substack{\text{S-alkyl thionitrite}\\ \text{(red)}}}{RCH_2{-}S{-}N{=}O} + H_2O$$

(iii) Hinsberg Test

- Based on the reaction of the amine with benzenesulfonyl chloride (Hinsberg reagent), it can be used to seperate 1°, 2°, and 3° amines.
- 1° amines: give solution that produce ppt after addition of HCl

$$\underset{\text{1° amine}}{RNH_2} + \underset{\substack{\text{benzenesulfonyl}\\ \text{chloride}}}{C_6H_5SO_2Cl} + 2NaOH \longrightarrow \underset{\text{(soluble)}}{C_6H_5SO_2NR^-Na^+} + NaCl + 2H_2O$$

$$\xrightarrow{H^+} \underset{\substack{\text{sulfonamide}\\ \text{(insoluble)}}}{C_6H_5SO_2NHR}$$

2° amines: give ppt - acidification of the solution does not dissolve the sulfonamide (i.e., the PPT is not soluble in NaOH or HCl)

$$\underset{2^\circ\text{ amine}}{R_2NH} + \underset{\text{benzenesulfonyl chloride}}{C_6H_5SO_2Cl} + NaOH \longrightarrow \underset{\text{sulfonamide (insoluble)}}{C_6H_5SO_2NR_2} + NaCl + H_2O$$

$$C_6H_5SO_2NR_2 \xrightarrow{H^+} \text{No Reaction}$$

- 3º amines: undergo reaction with benzenesulfonyl chloride to produce quaternary ammonium sulfonate salts, which yield sodium sulfonate and insoluble 3° amines in basic solution.
- Acidification of the reation mixture results in the formation of sulfonic acids and soluble amine salts

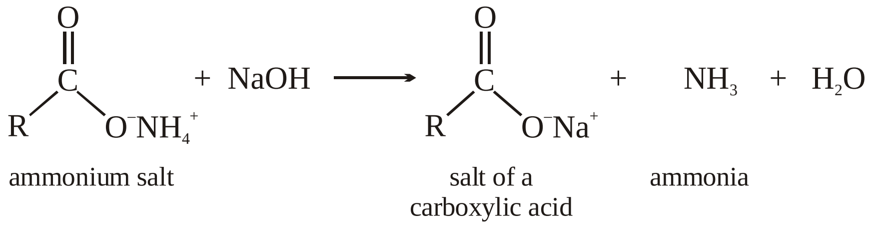
$$\underset{3^\circ\text{ amine}}{R_3N} + \underset{\text{benzenesulfonyl chloride}}{C_6H_5SO_2Cl} \longrightarrow C_6H_5SO_2NR_3^+Cl^- \xrightarrow{2NaOH}$$

$$\underset{\text{(soluble)}}{C_6H_5SO_3^-Na^+} + \underset{\text{(insoluble)}}{NR_3} + NaCl + H_2O \xrightarrow{2HCl} C_6H_5SO_3H + \underset{\text{(soluble)}}{R_3NH^+Cl^-} + 2NaCl$$

- The results of the Hinsberg test must not be used alone in classifying amines. The solubility of the original compounds must also be considered.
- If the original compound is amphoteric, which means that it is soluble in both acids and alkalies, the Hinsberg method fails to distinguish among the types of amines.

(iv) Sodium Hydroxide Treatment of Ammonium Salt and Amine Salts

- Amine salts can be detected by treating the salt with NaOH to liberate ammonia or amine.



$$\underset{\text{amine salt}}{RNH_3^+X^-} + NaOH \longrightarrow \underset{1^\circ\text{ amine}}{RNH_2} + NaX + H_2O$$

- Moistened pink litmus paper placed in the vapor above the solution will turn blue if ammonia or a volatile amine is present.

(v) Libermann's nitroso test :

It is used as a test for secondary amines.Secondary amines(aliphatic as well as aromatic) reacts with nitrous acid to form N-nitrosoamines.

$$(CH_3)_2NH + HONO \longrightarrow (CH_3)_2N\text{–}N = O + H_2O$$

- Nitrosoamines are water soluble yellow oils and when warmed with phenol and few dropos of conc.H_2SO_4 produce a green colour solution which turns blue on adding alkali.This reaction is called Libermann's nitroso reaction .
- Tertiary amine do not react with nitrous acid.

Sodium Metal :

- The active hydrogen on 1° and 2° amines undergo reaction with sodium to form salt and liberate hydrogen gas

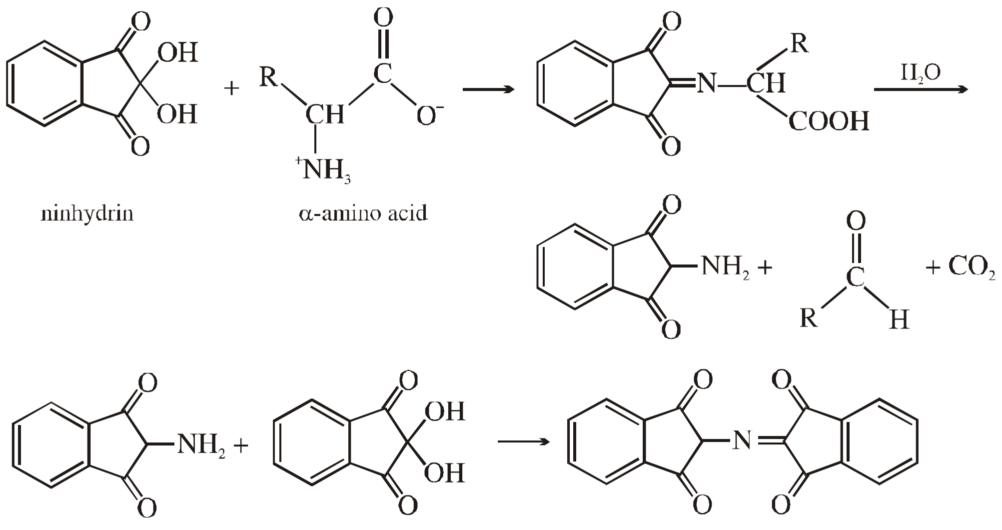
$$\underset{1^\circ\text{amine}}{2RNH_2} + 2Na \longrightarrow 2RNH^-Na^+ + H_2(g)$$

$$\underset{2^\circ\text{amine}}{2R_2NH} + 2Na \longrightarrow 2R_2N^-Na^+ + H_2(g)$$

7. Tests for Amino Acids

(i) Ninhydrin Test :

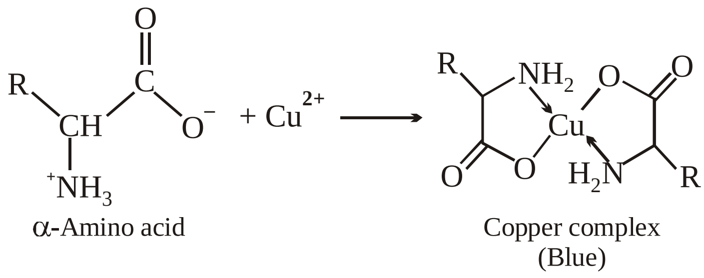
- Amino acids and p-amino acids react with ninhydrin to give a positive test which is blue or blue-violet color.



- Ammonium salts ($NH_4^+Cl^-$) give a positive test.
- Some amines, such as aniline, yield orange to red colors, which is considered a negative test.
- Proline, hydroxyproline, and 2-, 3-, and 4-aminobenzoic acids fail to give

Blue colour but produce a yellow color instead.

(ii) Copper Complex Formation



- Reaction with copper(II) sulfate solution yields a moderate-to deep-blue liquid or a dark-blue solid.

8. Tests for Aromatics

- If the molecule already contains reactive chemical substituents (acids, amines, ethers, carbonyl compounds, etc.,) use the corresponding classification test for that particular group.
- New substituents can be added onto the aromatic ring or existing substituents can be modified, such that the new

Compound May be More Readily Characterized.

(i) Fuming Sulfuric Acid

$$\underset{\text{aromatic compound}}{\mathrm{ArH}} \xrightarrow[\mathrm{SO_3}]{\mathrm{H_2SO_4}} \underset{\text{arylsulfonic acid}}{\mathrm{ArSO_3H}} + \text{heat}$$

- This test is good for aromatics with no other functional groups.
- Positive Test: the aromatic compound dissolves completely in H_2SO_4 with the evolution of heat (Fuming)

(ii) Chloroform and Aluminum Chloride

$$\underset{\substack{\text{aromatic}\\ \text{compound}}}{\mathrm{3ArH}} + \mathrm{CHCl_3} \xrightarrow{\mathrm{AlCl_3}} \underset{\text{triarylmethane}}{\mathrm{Ar_3CH}} + \mathrm{3HCl}$$

$$\underset{\text{triarylmethane}}{\mathrm{Ar_3CH}} + \mathrm{R^+} \longrightarrow \underset{\substack{\text{triaryl carbocation}\\ \text{(colored)}}}{\mathrm{Ar_3C^+}} + \mathrm{RH}$$

- Aromatics give colored solution or powder.
- Positive Test: (Orange, red, blue, purple, green)
- Non aromatics give yellow color (Negative result)

(iii) Azoxybenzene and Aluminum Chloride

- The color of the solution or precipitate is dependent on the functional groups present on the aryl group.
- Aromatic hydrocarbons and their halogen derivatives produce a deep-orange to dark-red color in solution or give a precipitate.
- Fused aromatic ring (such as naphthalene, anthracene, and phenanthrene) produce brown color.
- Aliphatic hydrocarbons give no color or, at most, a pale yellow.

9. Tests for Ethers

- Ethers are only a little more polar and slightly more reactive than either saturated hydrocarbons or alkyl halides
- Ethers form extremely explosive peroxides upon standing, specially when exposed to air and/or light. Liquid ethers that shows solid precipitates should not be handled.

(i) Hydroiodic Acid (Zeisel's, Alkoxyl method)

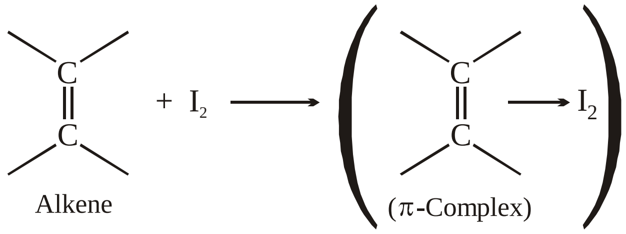
$$\underset{\text{ether}}{R'OR} + \underset{\text{hydroiodic acid}}{2HI} \longrightarrow \underset{\text{alkyl iodides}}{R'I + RI} + H_2O$$

$$\underset{\text{ether}}{ArOR} + \underset{\text{hydroiodic acid}}{HI} \longrightarrow \underset{\text{alkyl iodides}}{RI} + \underset{\text{phenol}}{ArOH}$$

$$\underset{\substack{\text{mercuric}\\\text{acetate}}}{Hg(NO_3)_2} + \underset{\substack{\text{alkyl}\\\text{iodide}}}{2R'I} \xrightarrow{H_2O} \underset{\substack{\text{mercuric}\\\text{iodide}\\\text{(orange)}}}{HgI_2} + 2R'OH + 2HNO_3$$

- Positive Test: Orange or Orange-red color indicating.
- Note: Ethyl and methyl esters give also positive result.

(ii) Iodine Test for Ethers and Unsaturated Hydrocarbons

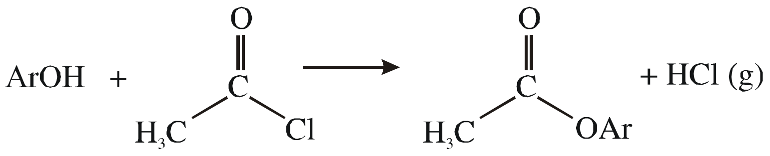


$$\underset{\text{ether}}{R_2\ddot{O}:} + I_2 \longrightarrow \left(R_2\ddot{O}: \longrightarrow I_2\right)$$

- Positive test: the color of the solution changes from purple to tan.
- Aromatic hydrocarbons, saturated hydrocarbons, fluorinated hydrocarbons and chlorinated hydrocarbons do not react.
- Unsaturated hydrocarbons produce alight-tan solid, while retaining the purple color of the iodine solution.

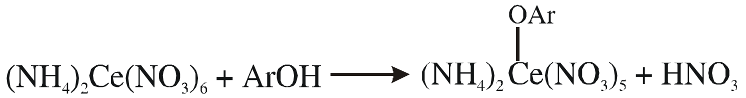
10. Tests for Phenols

- As with alcohols, the acidic hydrogen in phenol can be detected with sodium (hydrogen gas is evolved) or with acetyl chloride (an ester layer is formed).



Phenol Acetyl chloride ester

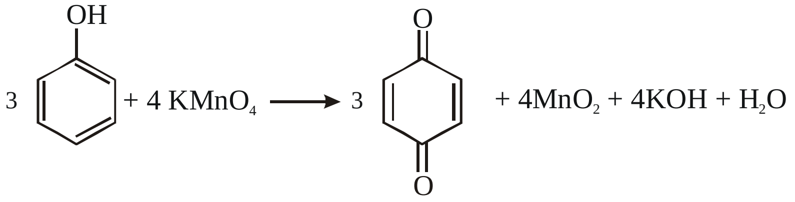
- Phenols undergo reaction with yellow ceric ammonium nitrate to produce brown or black products.



$$(NH_4)_2Ce(NO_3)_6 + ArOH \longrightarrow (NH_4)_2\overset{\overset{OAr}{|}}{Ce}(NO_3)_5 + HNO_3$$

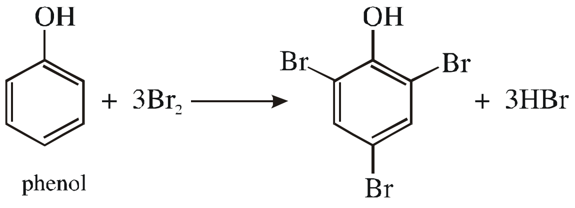
ceris ammonium nitrate (yellow) phenol (brown or black)

- Phenols reduce potassium permanganate solution and undergo oxidation to quinones.
- The manganese is reduced from +7 which gives a purple solution to +4 which is brown.



Phenol Phenol quinone brown

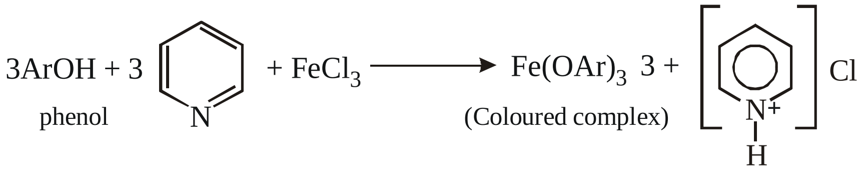
(i) Bromine water



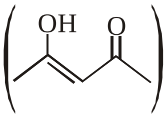
phenol 2,4,6-tribromophenol (white)

- Positive Test: decolorization of bromine.
- This is good for water soluble phenols

(ii) Ferric Chloride - Pyridene Reagent



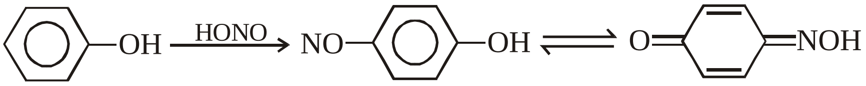
phenol (Coloured complex)

- Positive Test: Production of blue, violet, purple, green, or red-brown colors
- Good for all types of Ar-OH.
- Positive test for enols. 

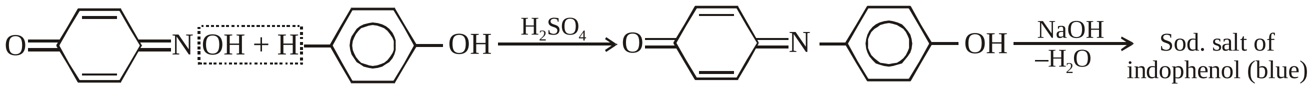
- Carboxylic acid with $FeCl_3$ gives red colour only when saturating with NH_3 .

(iii) Libermann's nitroso test :

While phenol is reacted with $NaNO_2$ and concentrated H_2SO_4, it provides a deep green colour which changes to red on dilution with water. while generated alkaline along with NaOH, blue colour is restored. This reaction is termed as Liebermann's nitroso reaction and is employed as a test of phenol.



p-Nitrosophenol Quinoxim



Indo phenol (Red)

11. Test For Nitro Compounds

(i) Ferrous Hydroxide Reduction

$$RNO_2 + 6Fe(OH)_2 + 4H_2O \longrightarrow RNH_2 + 6Fe(OH)_3$$

Nitroalkene Ferrous hydroxide (green) Ferric hydroxide (red-brown, brown)

- Positive Test: indicated by the change in color from green to red-brown or brown due to the oxidation of iron from+2 to +3.
- A negative test is indicated by a greenish precipitate.
- Note: Nitroso compounds, quinones, hydroxylomines alkyl nitrates give also positive results

(ii) Zinc and Ammonium Chloride Reduction

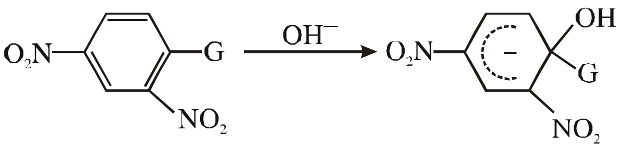
$$\underset{\text{Nitro compound}}{RNO_2 + 4[H]} \xrightarrow[NH_4Cl]{Zn} \underset{\text{Hydroxylamine}}{RNHOH} + H_2O$$

$$RNHOH + \underset{\text{Tollens reagent}}{2Ag(NH_3)_2OH} \longrightarrow RNO + 2H_2O + 2Ag(S) + 4NH_3$$

- Test the solution with Tollens Reagent
- **<u>Positive Test</u>**: formation of metallic silver
- Only 3° aliphatic nitro compounds and aromatic nitro compounds are reduced by Zn/NH_4Cl to the hydroxylamine.
- The hydroxylamine is then detected by the formation of metallic silver in the Tollens test (or formation of a black or grey precipitate). This is known as Mulliken–baker test:.

(iii) Treatment of Aromatic Compounds with Sodium Hydroxide

- The number of nitro groups on an aromatic ring can be determined by the reaction with NaOH
- In the reaction with NaOH:
- Mononitro aromatic compounds yield no color change or a very light yellow
- Dinitro aromatic compounds produce a bluish-purple color
- Trinitro aromatic compounds give a red color
- The color of the solution is due to a Meisenheimer complex



Meisenheimer complex