

Stereochemistry

Chemistry in Three Dimensions

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Isomers – different compounds with the same molecular formula.

Structural Isomers – isomers that differ in which atoms are bonded to which atoms.

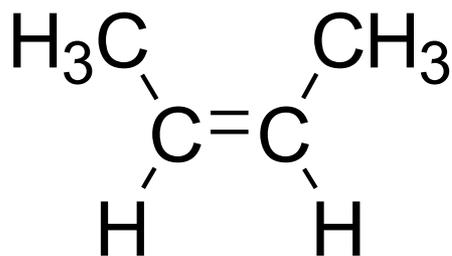
eg. C_4H_{10}

$CH_3CH_2CH_2CH_3$
n-butane

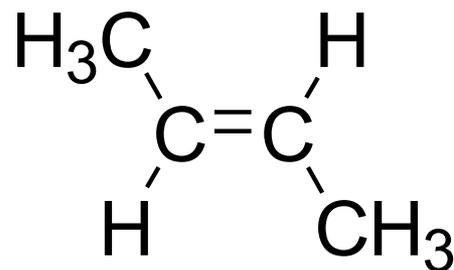
CH_3
 CH_3CHCH_3
isobutane

Stereoisomers – isomers that differ in the way the atoms are oriented in space, but not in which atoms are bonded to which atoms.

eg. *cis*-2-butene



trans-2-butene



Stereochemistry:

importance:

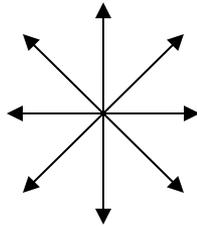
biochemicals

medicine

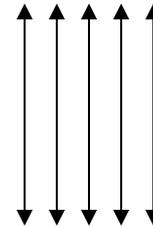
tool for studying mechanisms

optical activity – when a substance rotates the plane of plane polarized light. (1815 by Biot)

plane polarized light – light that has been passed through a nicol prism or other polarizing medium so that all of the vibrations are in the same plane.

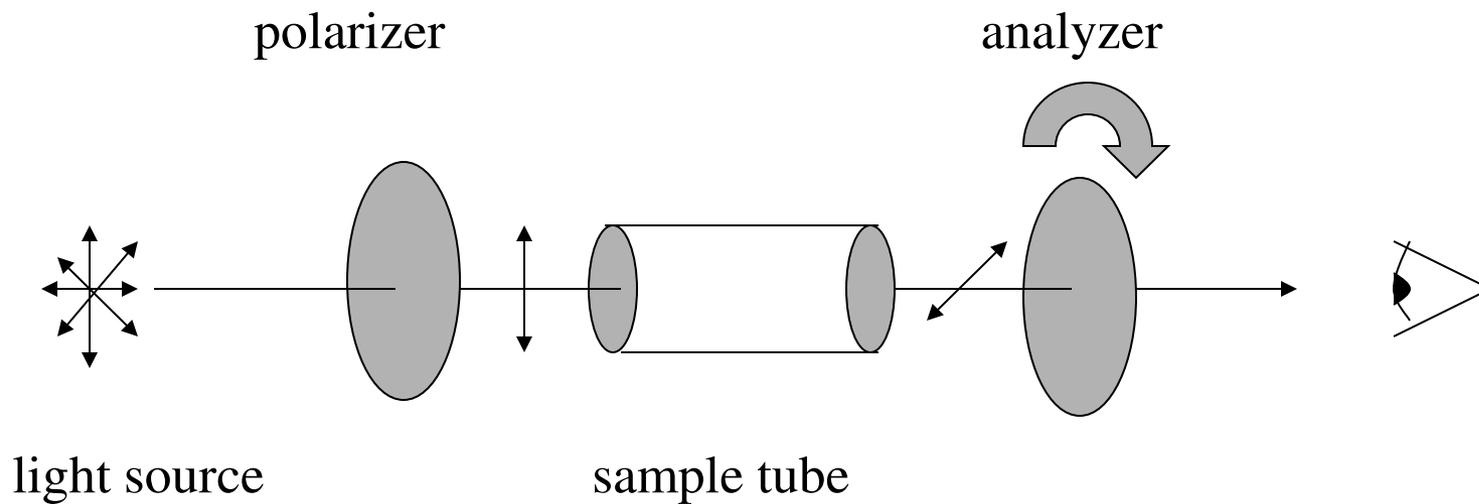


non-polarized



polarized

polarimeter – an instrument used to measure optical activity.



dextrorotatory – when the plane of polarized light is rotated in a clockwise direction when viewed through a polarimeter.

(+) or (*d*) do not confuse with D

levorotatory – when the plane of polarized light is rotated in a counter-clockwise direction when viewed through a polarimeter.

(-) or (*l*) do not confuse with L

The angle of rotation of plane polarized light by an optically active substance is proportional to the number of atoms in the path of the light.

specific rotation – the angle of rotation of plane polarized light by a 1.00 gram per cm^{-3} sample in a 1 dm tube. $[\alpha]_D$ (D = sodium lamp, $\lambda = 589 \text{ m}\mu$).

$$[\alpha]_D = \frac{\alpha}{l * d} \quad \text{where } \alpha = \text{observed rotation}$$

$l = \text{length (dm)}$
 $d = \text{concentration (g/cc)}$

(+)-alanine $[\alpha]_D = +8.5$

(-)-lactic acid $[\alpha]_D = -3.8$

Why are some substances optically active and others not? Can we predict which ones will be and which ones won't?

Louis Pasteur (1848) recrystallized sodium ammonium tartrate (optically inactive). He noticed that the crystals were of two types which he physically separated. The two types of crystals were optically active, but rotated the plane of polarized light in opposite directions. He proposed that the molecules came in two forms, "left handed" and "right handed". Together, the mixture of the two forms is optically inactive.

enantiomers - mirror-image stereoisomers.

The physical and chemical properties of enantiomers are identical, except 1) the direction of rotation of the plane of plane polarized light and 2) how they react with optically active reagents.

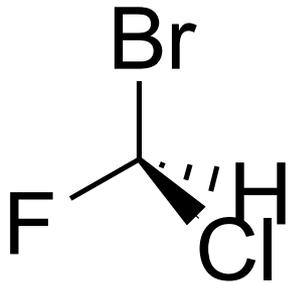
chiral center— is a carbon that is bonded to four different groups of atoms. (do not confuse with “chiral”)



configuration – the arrangement in space of the four different groups about a chiral center.

How do we show configurations?

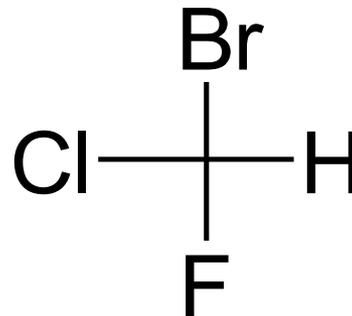
“wedge” formulas



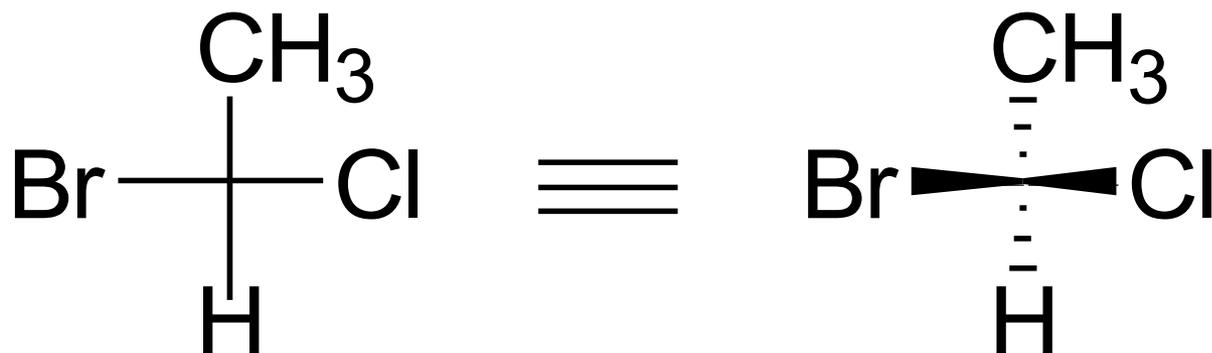
Fischer projections

“cross structures”

use only for chiral centers!



In the Fischer projection, the horizontal bonds to the chiral center are always above the plane and the vertical bonds to the chiral center are below the plane. (the horizontals are “hugging you.”)



chiral – not superimposeable on the mirror image
 (“handedness”)

achiral – superimposeable on the mirror image; not chiral.

Test for optical activity: chiral molecules are optically active.

racemic modification – equimolar molar mixture of enantiomers (will be optically inactive) (\pm).

- compounds with one chiral center will show optical activity
- compounds without chiral centers do not normally show optical activity
- compounds with more than one chiral center may or may not show optical activity depending on whether or not they are non-superimposable on their mirror image (chiral) or superimposable (achiral).

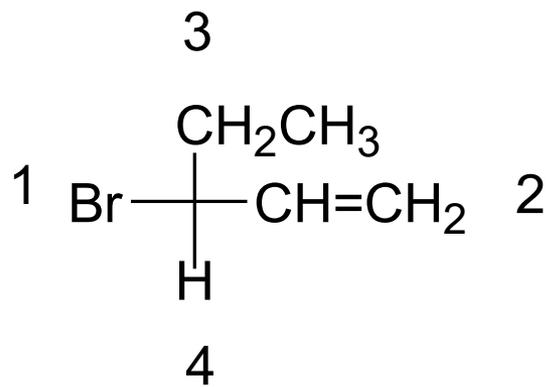
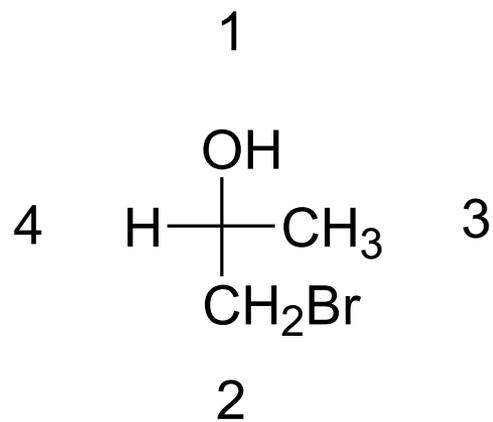
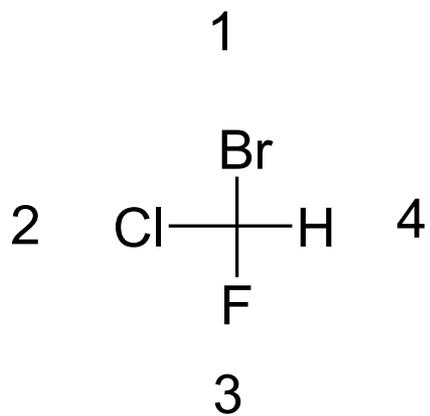
specification of configuration: The **R/S system**.

Cahn, Ingold, Prelog sequence rules:

sequence rule 1: the atom attached to the chiral center with the highest atomic number = 1, next = 2, etc.

sequence rule 2: if the four atoms attached to the chiral center are not all different, the sequence is determined at the first point of difference.

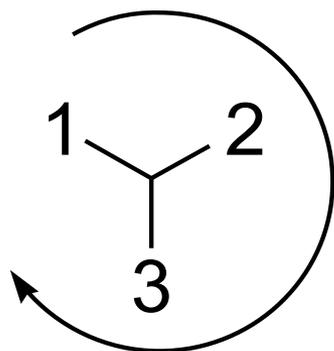
sequence rule 3: =X is equal to two -X, etc.



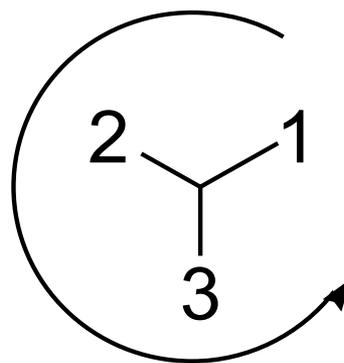
R/S:

1. Using the Cahn, Ingold, Prelog sequence rules, assign numbers to each of the four groups attached to the chiral center.
2. Rotate the number 4 group away from you and observe the sequence $1 \rightarrow 2 \rightarrow 3$ for the remaining groups.
3. If going from $1 \rightarrow 2 \rightarrow 3$ is clockwise, then the configuration is R (rectus). If the sequence $1 \rightarrow 2 \rightarrow 3$ is counter-clockwise, then the configuration is S (sinister).

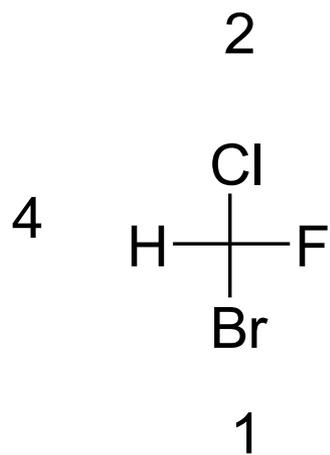
With group #4 rotated away:



R

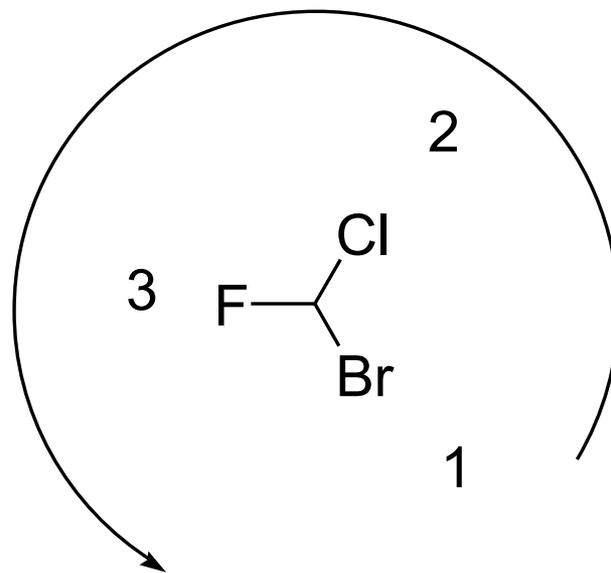


S



3

rotate #4 away



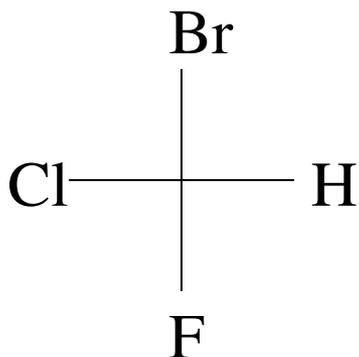
(S)-configuration

Using R/S problems on the web:

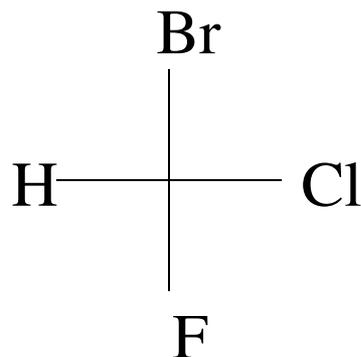
<http://chemistry2.csudh.edu/organic/startnewrands.html>

Angew. Chem. Int. Ed. Engl. **36**, 1057 (1997).

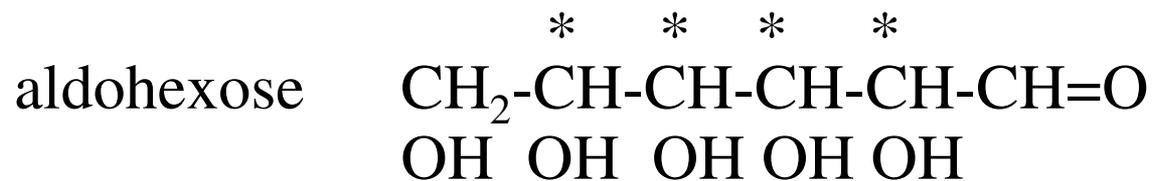
absolute configuration for bromochlorofluoromethane:



(R)-(-)-



(S)-(+)-

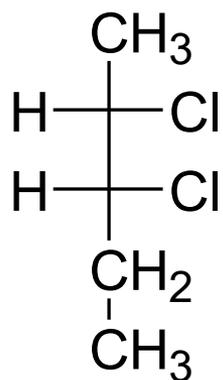


n chiral centers $\rightarrow 2^n$ maximum stereoisomers

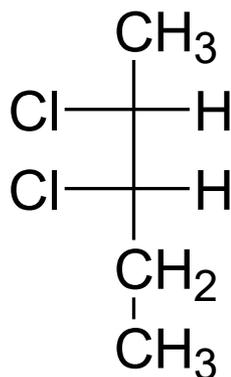
n = 4 $\rightarrow 2^4 = 16$ stereoisomers



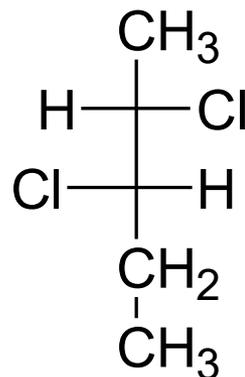
n = 2 $\rightarrow 2^2 = 4$ stereoisomers



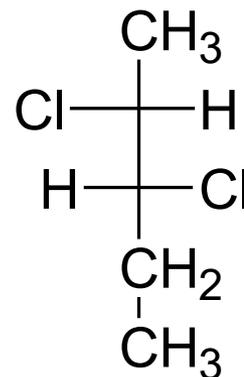
I



II



III

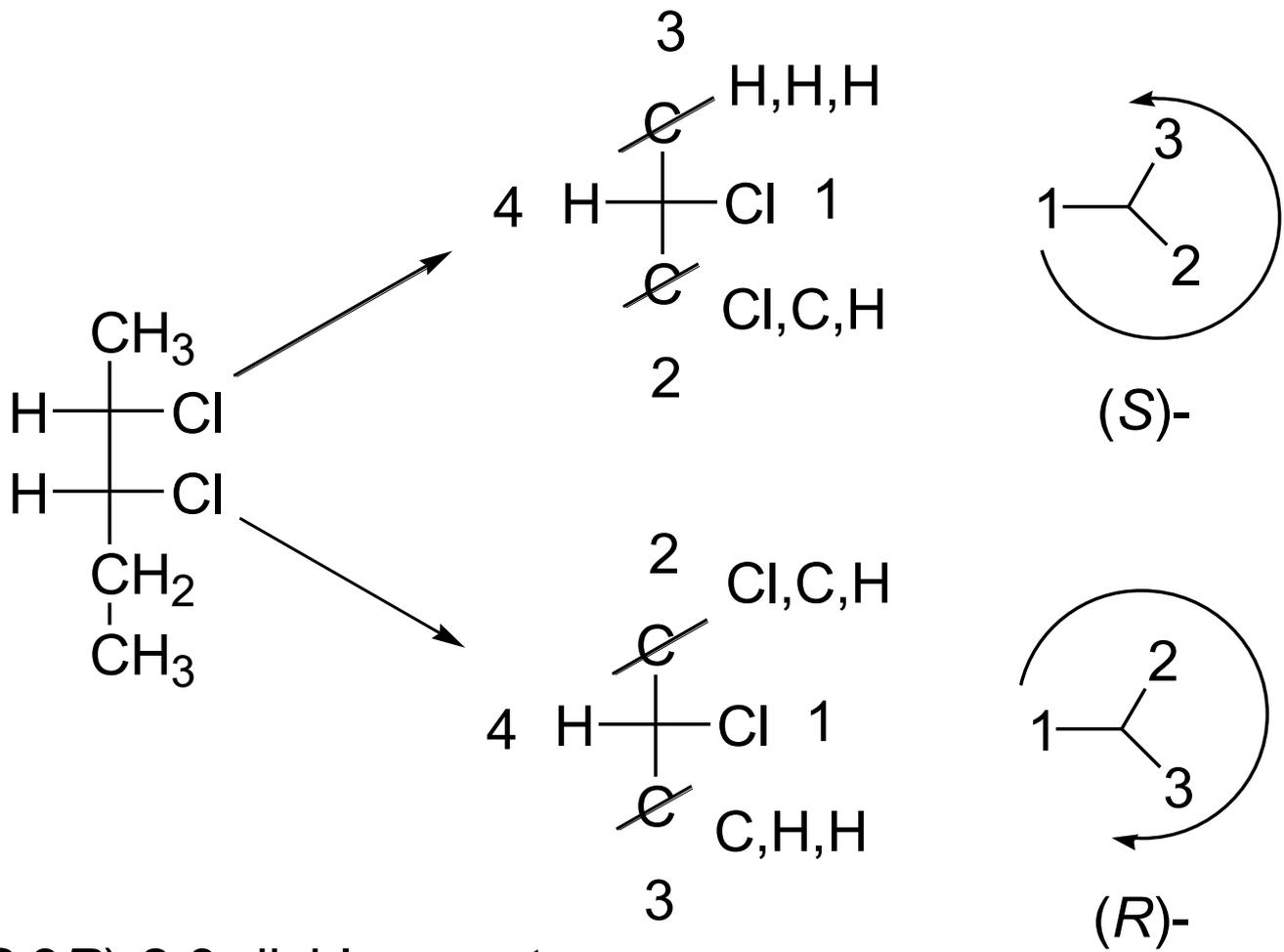


IV

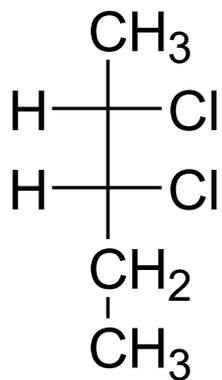
I & II are enantiomers; III & IV are enantiomers; I & III are diastereomers; I & IV are diastereomers...

diastereomers – non-mirror image stereoisomers.

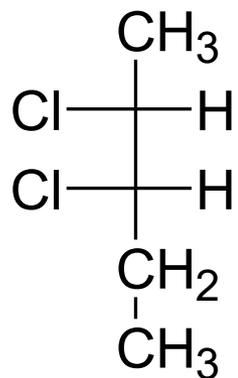
(the physical and chemical properties of diastereomers are different.)



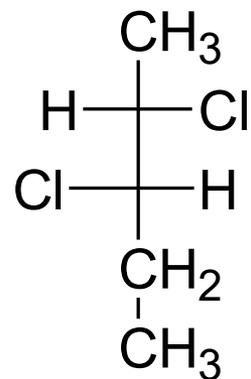
(2*S*,3*R*)-2,3-dichloropentane



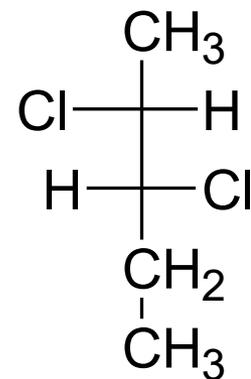
$(2S,3R)$ -



$(2R,3S)$ -

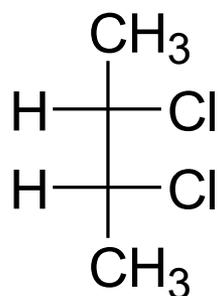


(S,S) -

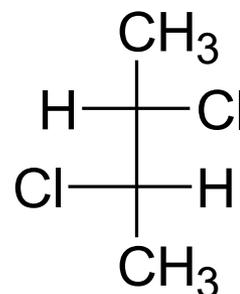
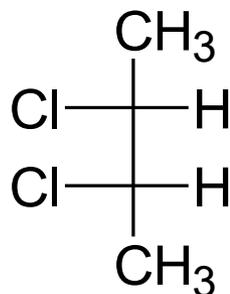


(R,R) -

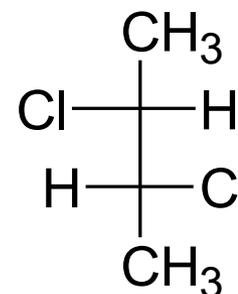
2,3-dichlorobutane



↑
I



II



III

***meso*-compound** – a compound that has chiral centers but is not chiral (optically inactive).

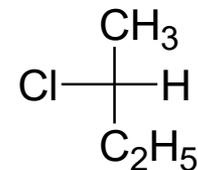
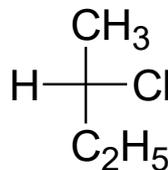
Reactions involving stereoisomers:

(a) the conversion of an achiral molecule into a chiral molecule, with the generation of a chiral center.



achiral

chiral



(S)-(+)-sec-butyl chloride

(R)-(-)-sec-butyl chloride

product is optically inactive \rightarrow racemic modification

The synthesis of chiral compounds from achiral reactants always yields the racemic modification.

Why? \ddagger R is enantiomeric to \ddagger S

$$\text{Eact (R)} = \text{Eact (S)}$$

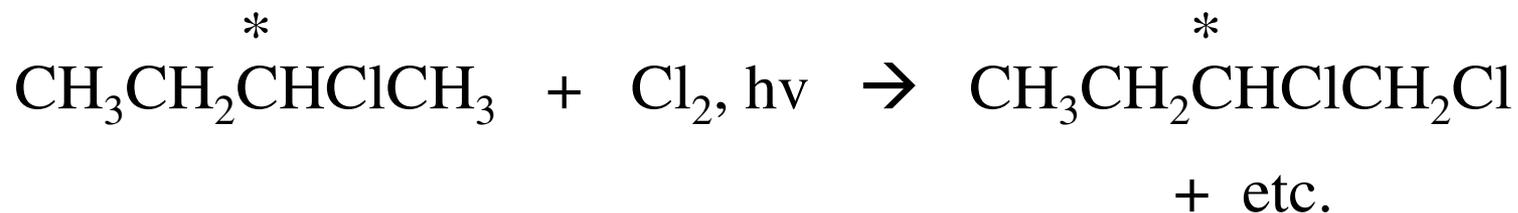
$$\text{rate (R)} = \text{rate (S)}$$

→ equimolar amounts

racemic modification

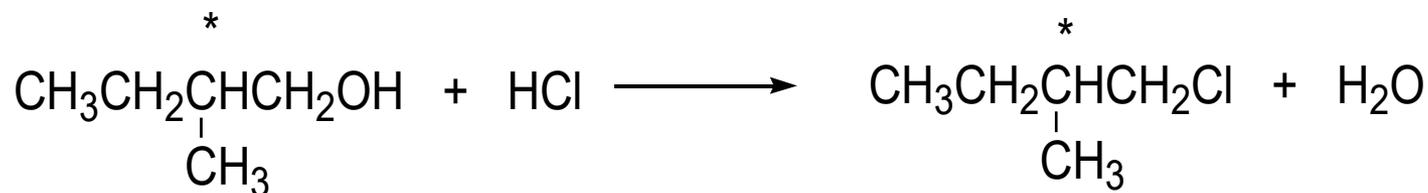
optically inactive

(b) reaction of a chiral molecule where bonds to the chiral center are not broken.

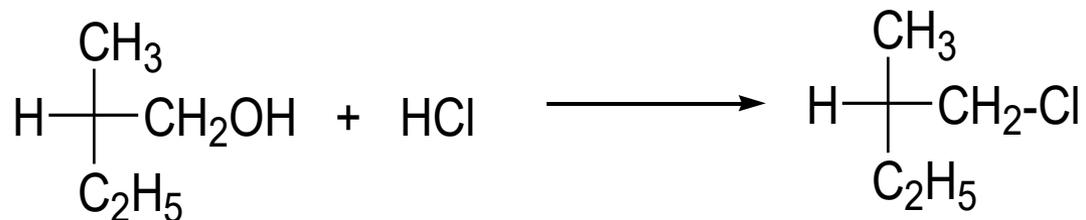


A reaction that does not involve the breaking of a bond to a chiral center proceeds with retention of configuration about the chiral center.

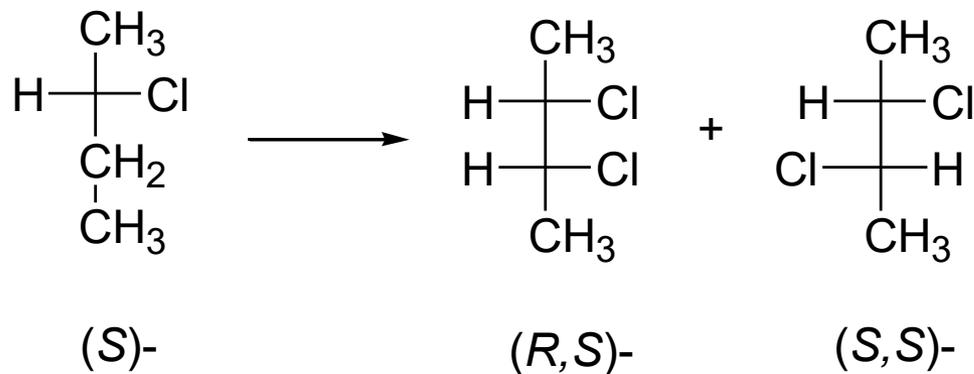
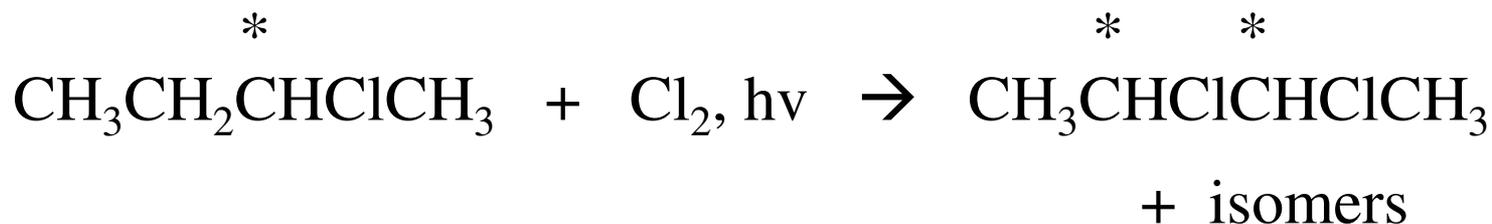
Can be used to “relate” configurations. If a compound can be synthesized by such a reaction from a compound of known configuration, then the configuration is known in the product.



It is known from X-ray crystallography that (-)-2-methyl-1-butanol is the (S)-isomer. When pure (-)-2-methyl-1-butanol is reacted with HCl, the product is dextrorotatory. Since no bonds to the chiral center were broken in the reaction, the (+)-1-chloro-2-methylbutane is now known to be the (S)-isomer.



(c) reactions like (b) in which a second chiral center is generated:



diastereomers in unequal amounts

The transition states are “diastereomeric”, the Eact’s are not equal, the rates are different.

(d) reactions of chiral compounds with optically active reagents.

Enantiomers have the same physical properties and cannot be separated by normal separation techniques like distillation, etc.

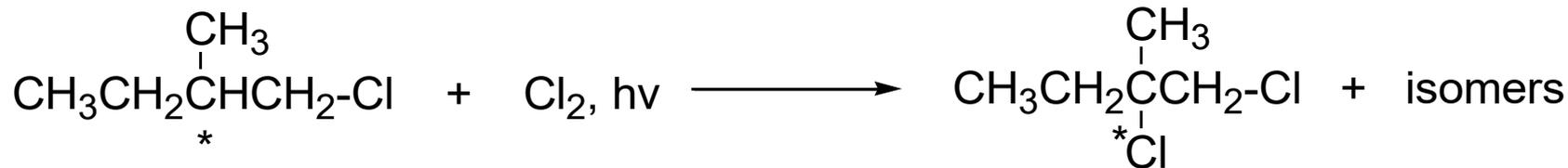
Enantiomers differ in reaction with optically active reagents.

Enantiomeric acids or bases can be reacted with an optically active base or acid to form salts that are diastereomers. Since diastereomers have different physical properties they can be separated by physical methods. The salts can then be converted back into the free acids or bases.

Resolution – the separation of enantiomers.

(e) a reaction of a chiral compound in which a bond to a chiral center is broken...

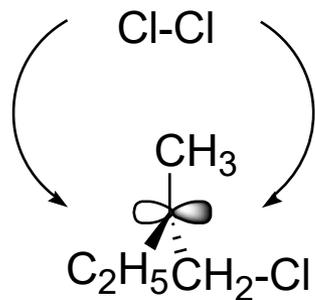
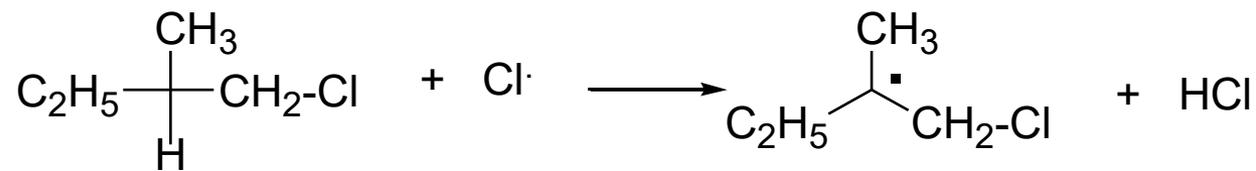
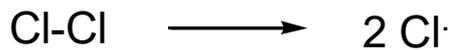
In a reaction of a chiral compound in which a bond to a chiral center is broken, the stereochemistry depends on the mechanism of the reaction.



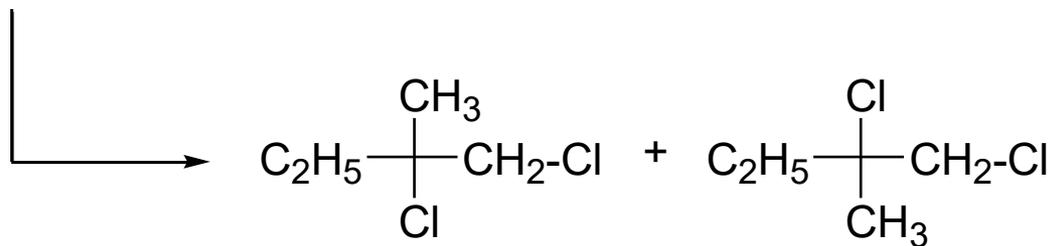
(S)-(+)-1-chloro-2-methylbutane

racemic-1,2-dichloro-2-methylbutane

optically inactive mixture



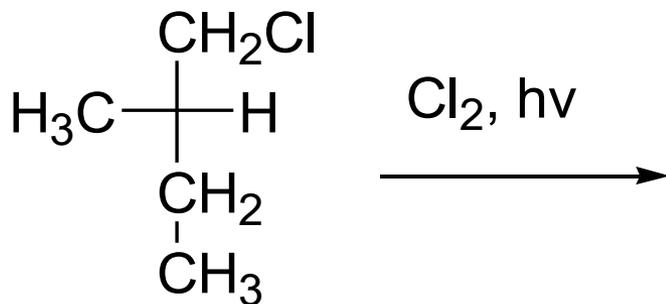
sp^2 hybridized flat free radical



In a reaction of a chiral compound in which a bond to a chiral center is broken, the stereochemistry depends on the mechanism of the reaction. This means that we can use the stereochemistry of such a reaction to give us information about the mechanism for that reaction.

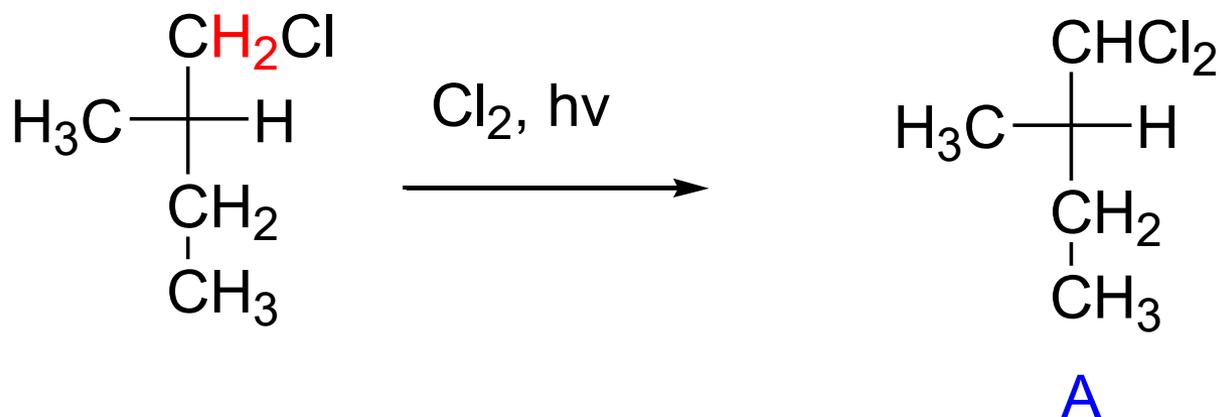
Homework problem 4.24

“Altogether, the free radical chlorination of (*S*)-(-)-1-chloro-2-methylbutane gave six fractions of formula $C_5H_{10}Cl_2$. Four fractions were found to be optically active, and two fractions optically inactive. Draw structural formulas for the compounds making up each fraction. Account in detail for optical activity or inactivity in each case.”

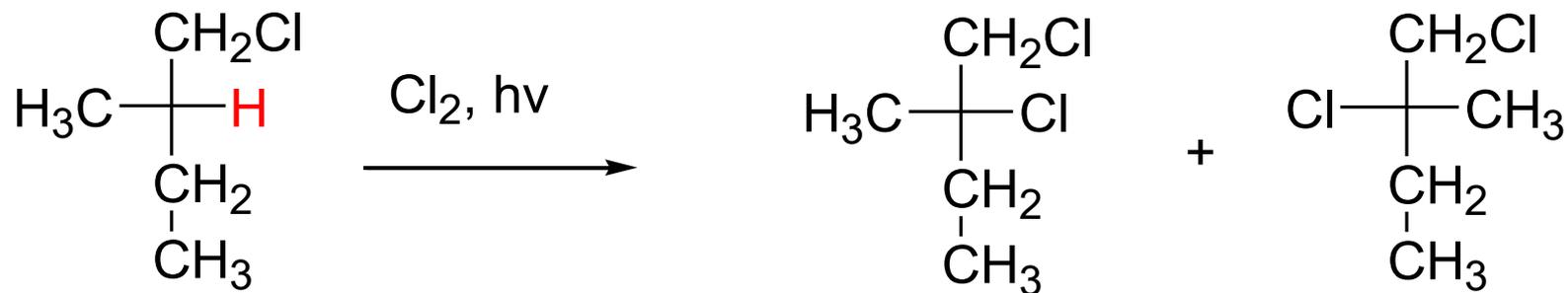


(S)-(-)-1-chloro-2-methylbutane

six fractions:
 four optically active
 two optically inactive

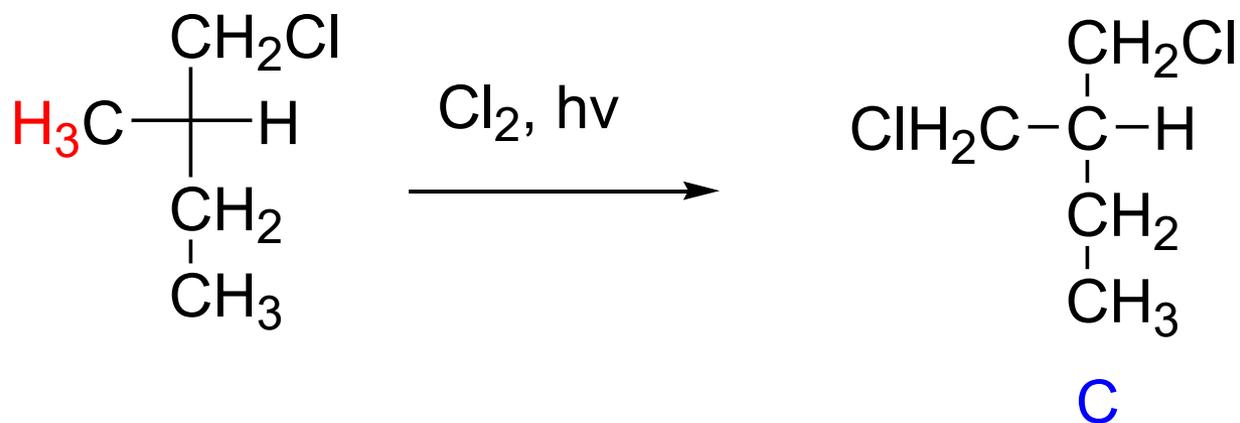


No bonds to the chiral center are broken, configuration is retained. Product is **optically active**

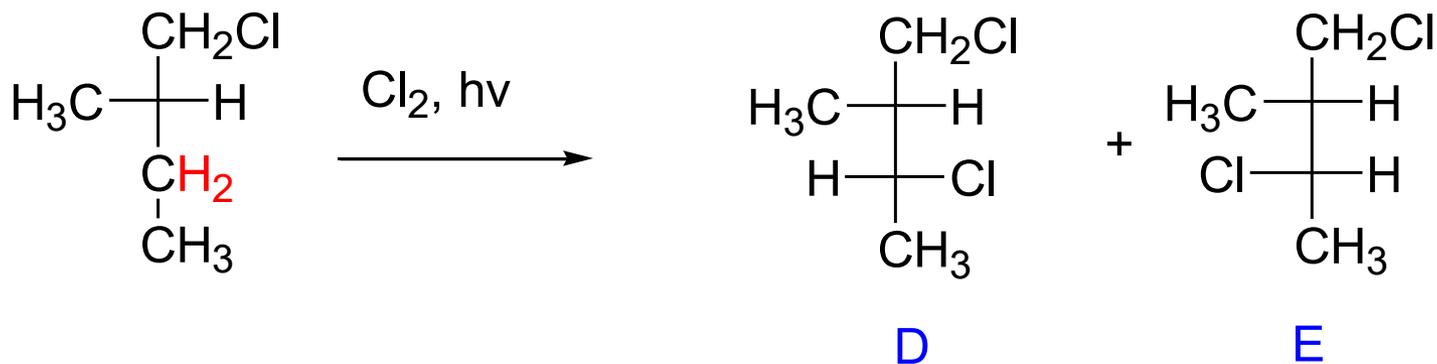


B

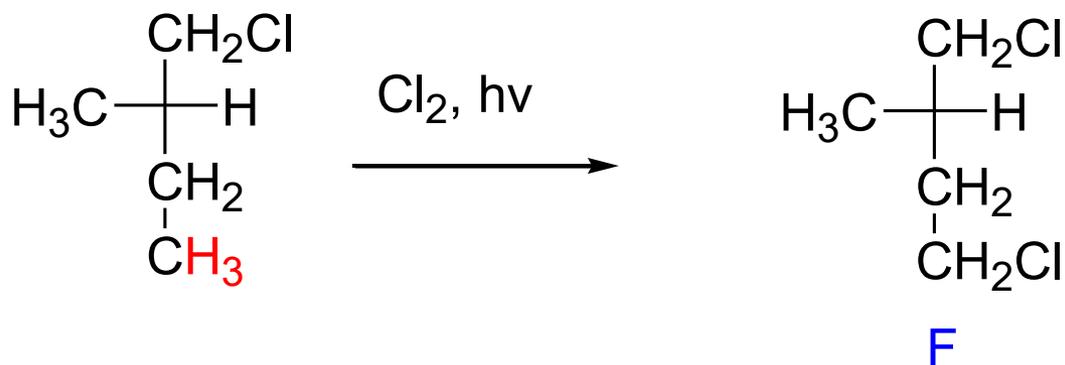
A bond is broken to the chiral center. Stereochemistry depends on the mechanism. Here, the intermediate free radical is flat and a racemic modification is formed. This fraction is optically inactive.



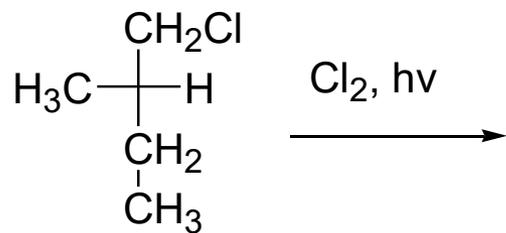
The product no longer has a chiral center. It is achiral and **optically inactive**.



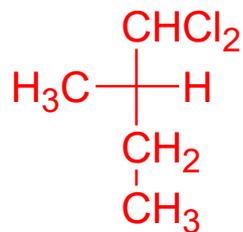
No bond is broken to the chiral center and a new chiral center is formed. The products are diastereomers and **each fraction is optically active.**



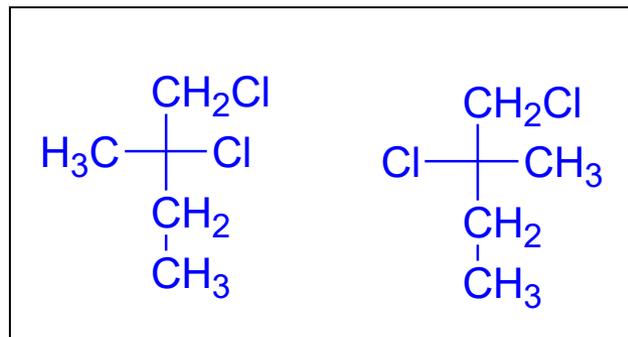
No bonds to the chiral center are broken, configuration is retained. Product is **optically active**



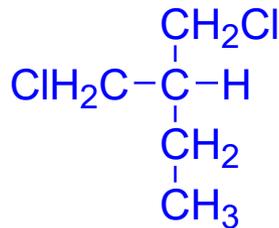
(S)-(-)-1-chloro-2-methylbutane



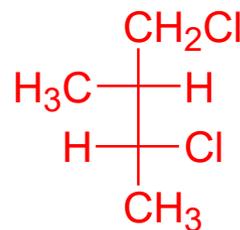
A



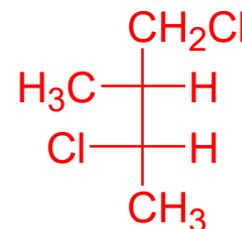
B



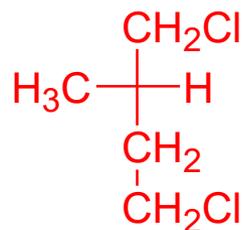
C



D



E



F

optically active
optically inactive



E-CONTENT PRESENTATION

on

FOOD ADULTERATION

For

PROJECT IN DEVELOPMENT OF E-CONTENT

(Faculty Development Program, 30th May to 4th June 2022)

Organized By

Department of Higher Education, Bhopal,
Govt. of Madhya Pradesh

Presented By

Dr. NEETUPRIYA LACHORIA

Assistant Professor, Chemistry

**Govt. Dr. Shyama Prasad Mukherjee Science & Commerce College,
Bhopal M.P.**

Students will be able to learn:

- **WHAT IS FOOD ADULTRATION ?**
- **WHY FOOD ADULTRATION IS DONE ?**
- **METHODS OF FOOD ADULTRATION ?**
- **HOW CAN ADULTRATION BE PREVENTED ?**

INTRODUCTION

- Food Adulteration has become a very common practice in our country and we are consuming these food almost everyday, which have numerous harmful effects to our health. Everyday we go through the news how the unhygienic and spurious foods are entering into our houses. Adulteration of foods has many effects on individuals as well as on the community health.
- Food adulteration is a social evil. It consist of a larger number of practice like mixing, substitution, misbranding, putting up decomposed food for sale.

WHAT DOES ADULTERATION MEAN?

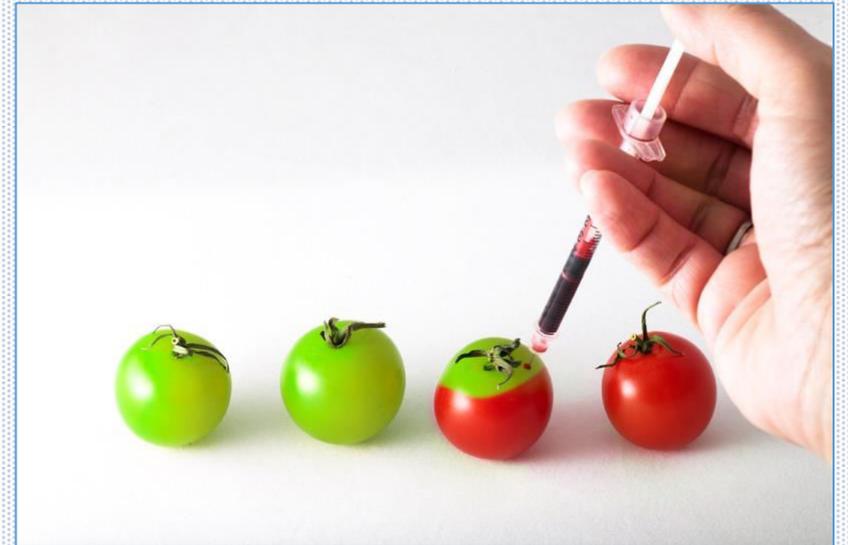
- Adulteration is addition or subtraction of anything from the food which affects its nutritional value for unfair economic gain. Adulteration of food is done in the following manners:
 - Mixing
 - Exchanging the main principle in the food articles
 - Removing something from the original food
 - Misbranding or cheating by similar name
 - Mislabeleding

WHY FOOD ADULTRATION IS DONE ?

- Practiced as a part of business strategy.
- An imitation of some other food substance.
- Lack of knowledge.
- To increase the quantity of food production and sales.
- Increased food demand for a rapidly growing population.
- To make maximum profit from food items by fewer investments.
- Lack of consciousness of proper food consumption
- Lack of effective food laws

TECHNIQUES USED FOR FOOD ADULTERATION

- Mixing other ingredients.
- Substitution of the food stuffs by another.
- Abstraction of an amount from a food stuffs.
- Concealing food quality.
- Selling decomposed food.
- Adding toxic substance.
- Selling inferior quality of food using brand name.



COMMONLY ADULTERATED FOODS

FOOD MATERIAL

- Cereals
- Dais
- Turmeric powder
- Black pepper
- Chili powder
- Tea dust
- Ghee
- Coffee powder
- Mustard seeds

ADULTERATE ITEMS

- Mud, soap stones, grit
- Coal tar dye, kesari dal
- Lead chromate powder
- Papaya seed
- Saw dust
- Black gram husk
- Vanaspati
- Chicory , date husk
- Small stones

PREVENTION FROM FOOD ADULTERATION

- No to adulterated cold drinks
- Parents should be concerned about the quality and freshness of the food articles like chocolates, sweets that children usually like.
- Take the help of the food adulteration testing centres. Lodge complaints to the concerned authorities, if adulteration is detected.
- Make sure that food packets carry ISI, AGMARK or FPO labels.
- Always check for packaging date and expiry date of the product.

LEARN MORE

- **Book on Food Adulteration by Frank Weiss**
- https://youtu.be/l0BthUI_MMA
- <https://youtu.be/e-UKv6TA-G0>

ASSESSMENT

Choose the Correct Answer

1. Which of the following is an adulterant in milk?

(A) Pebbles

(B) Urea

(C) Lead

(D) Oil

2. The addition of certain undesired substances to the food leads to the contamination of food. These are collectively called as:

(A) Adulterants

(B) Nutrients

(C) Minerals

(D) Consumption

3. Addition of these adulterants reduces the value of In food.

(A) Quantity

(B) Quality

(C) Nutrients

(D) Substance

Thank
You

UV-VISIBLE SPECTROSCOPY



Department of Chemistry

Govt Dr Shyama Prasad Mukharjee Science and Commerce
College [Old Benazeer College]

UV-VISIBLE SPECTROSCOPY

Presented By

Dr. Sudhanshu dhar

Dwivedi

Learning objectives

You will be able to

- ❑ Explain the instrumentation & working of UV-visible spectroscopy.
- ❑ Explain the electronic transition.
- ❑ List out the application of UV-visible spectroscopy.

Contents

- ▣ History
- ▣ Introduction
- ▣ Beer-Lambert law
- ▣ Electro magnetic spectrum
- ▣ Electronic transition
- ▣ Instrumentation
- ▣ Application
- ▣ Advantages & disadvantages

HISTORY

- ▣ In July 1941, Arnold Beckman, founder of his eponymous company, introduced his DU UV-visible spectrometer. It was the production version of the model D prototype that he and Howard Cary had first built.

It featured a molecular hydrogen lamp, a monochromator made of a Brazilian quartz prism, and a UV-sensitive phototube. Light from the lamp passed through a series of slits and mirrors and separated into the complete visible and UV spectrum at the prism. Once through the sample, the light collected in a phototube for measurement.

Uv visible spectroscopy



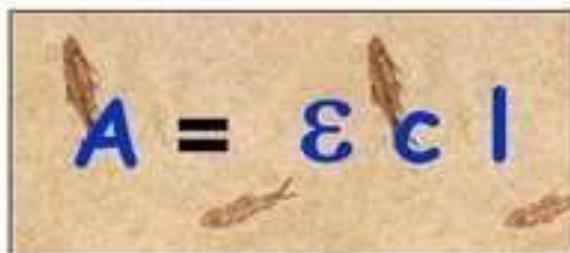
Introduction

- ▣ UV-visible spectroscopy is the measurement of the wavelength and intensity of absorption of near – ultraviolet and visible light by a sample.
- ▣ Ultraviolet and visible are energetic enough to promote outer electrons to higher energy levels .
- ▣ UV- visible spectroscopy is usually applied to molecules and inorganic ions or complexes in solution.
- ▣ The UV –visible spectra have broad features that are limited use for sample identification but are very useful for quantities measurements .
- ▣ The concentration of an analyte in solution can be determined by measuring the absorbance at some wavelength and applying the beer-Lambert law.

BEER- LAMBERT LAW

- When a monochromatic light of initial intensity I° passes through a solution in a transparent vessel, some of the light is absorbed so that the intensity of the transmitted light I is less than I° . There is some loss of light intensity from scattering by particles in the solution and reflection at the interfaces, but mainly from absorption by the solution.
- The relationship between I and I° depends on the path length of the absorbing medium, l , and the concentration of the absorbing solution, C . These factors are related in the laws of Lambert and Beer.

Beer-Lambert Law


$$A = \epsilon c l$$

A = absorbance (no units).

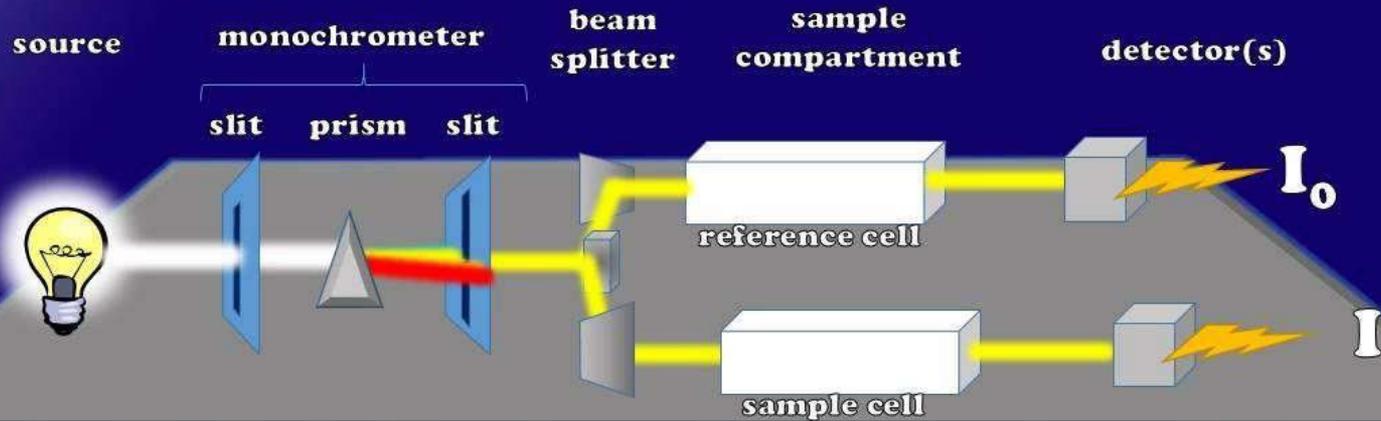
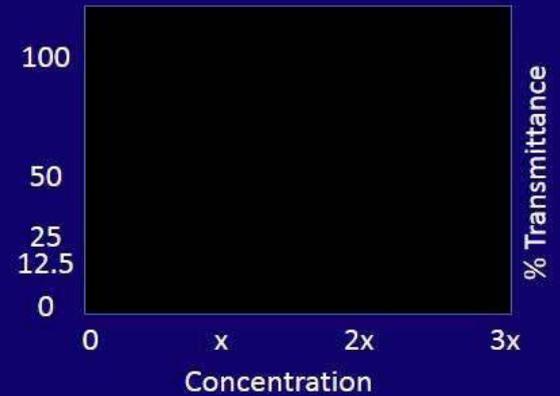
ε = Molar extinction coefficient ($M^{-1} \text{ cm}^{-1}$).

c = Concentration (M).

l = pathlength (cm).

Beer Lambert law

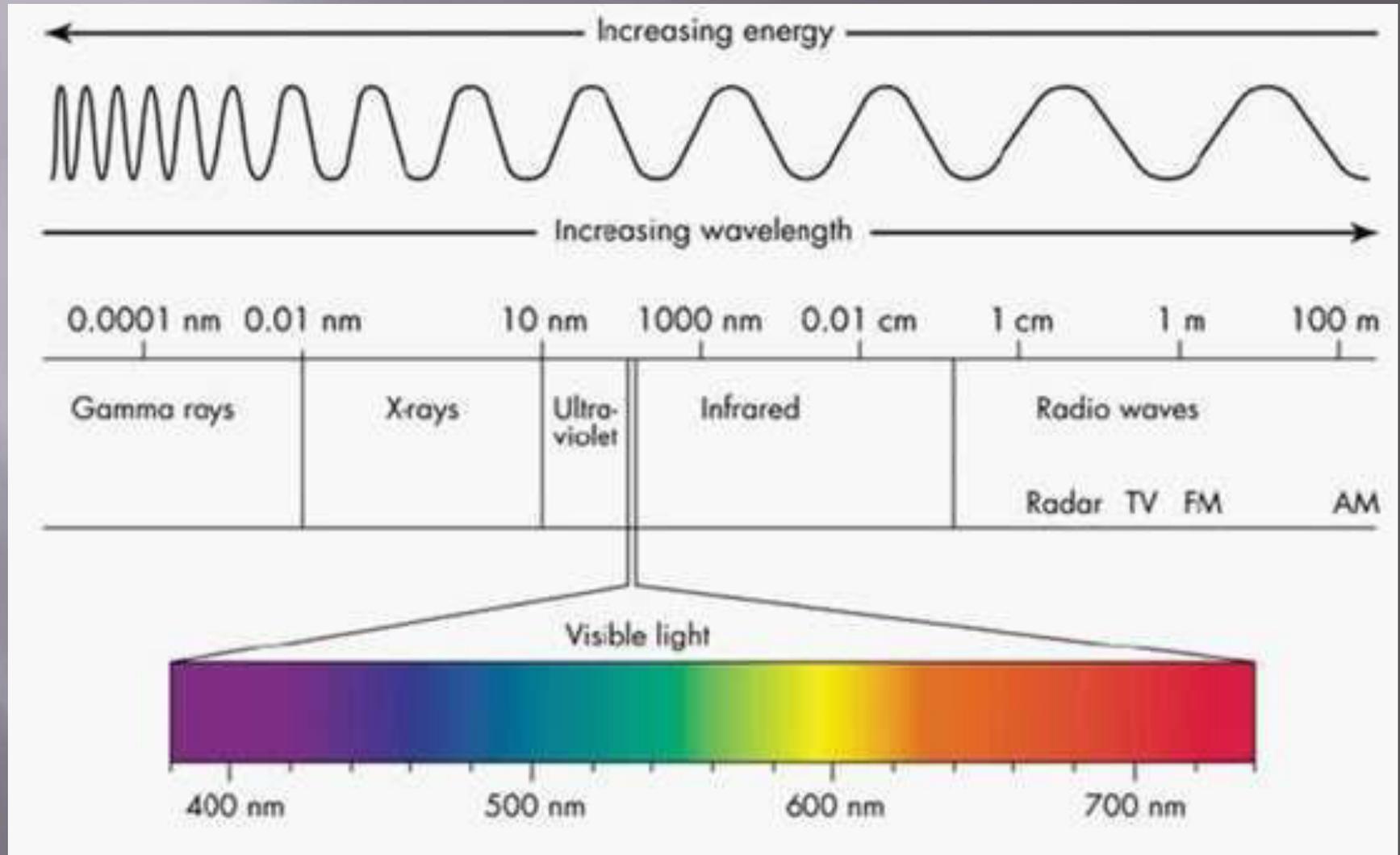
UV-visible Spectroscopy and the Beer-Lambert Law



Limitation

- ▣ The Beer's law is rigorously obeyed provided a single species gives rise to the observed absorption. However, the law may not be obeyed when.
 1. Different forms of the absorbing molecules are in equilibrium.
 2. Solute and solvent form association complexes.
 3. There is a thermal equilibrium between ground electronic state and excited state.
 4. The compounds are charged by irradiation
 5. High concentration-particles too close.

Electro magnetic spectrum



What is UV visible spectroscopy?

- Absorption of light in the UV/Visible part of the spectrum (210 – 900 nm)
- The transitions that result in the absorption of electromagnetic radiation in this region of the spectrum are transitions between electronic energy levels.
- Generally, the most probable transition is from highest occupied molecular orbital (HOMO) to lowest occupied molecular orbital (LUMO).

chromophore

- ▣ The term chromophore was previously used to denote a functional group or some other structural feature of which gives a color to a compound.
- ▣ For example, nitro group is a chromophore because its presence in a compound gives yellow color to the compound.
- ▣ Any group which exhibits absorption of electromagnetic radiation in a visible or UV region, it may or may not impart any color to the compound.
- ▣ Chromophores are ethylene, acetylene, carbonyls, acids, ester.

Auxochrome

- ▣ An auxochrome is a functional group of atoms attached to the chromophore which modifies the ability of the chromophore to absorb light, altering the wavelength or intensity of the absorption
- ▣ Example, Beta carotene



Absorption and intensity shifts

- ▣ Bathochromic shift (red shift): a shift to lower energy or longer wavelength.
- ▣ Hypsochromic shift (blue shift): a shift to higher energy or shorter wavelength.
- ▣ Hyperchromic effect: An increase in intensity.
- ▣ Hypochromic effect: A decrease in intensity

Ultraviolet-Visible Spectroscopy

Absorption and Intensity Shifts

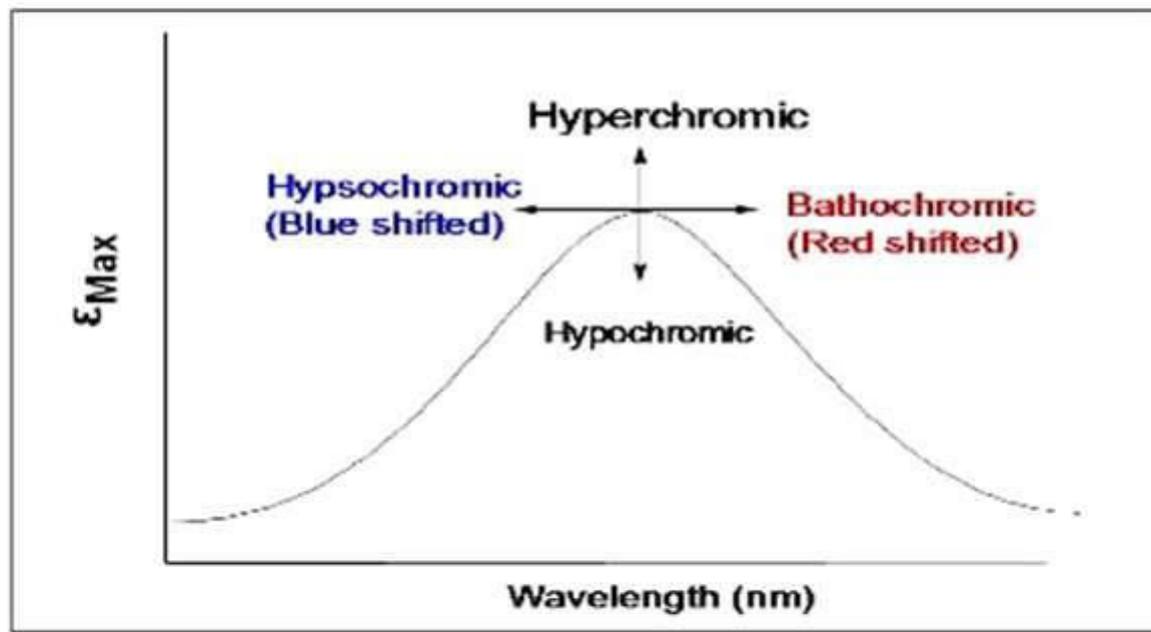
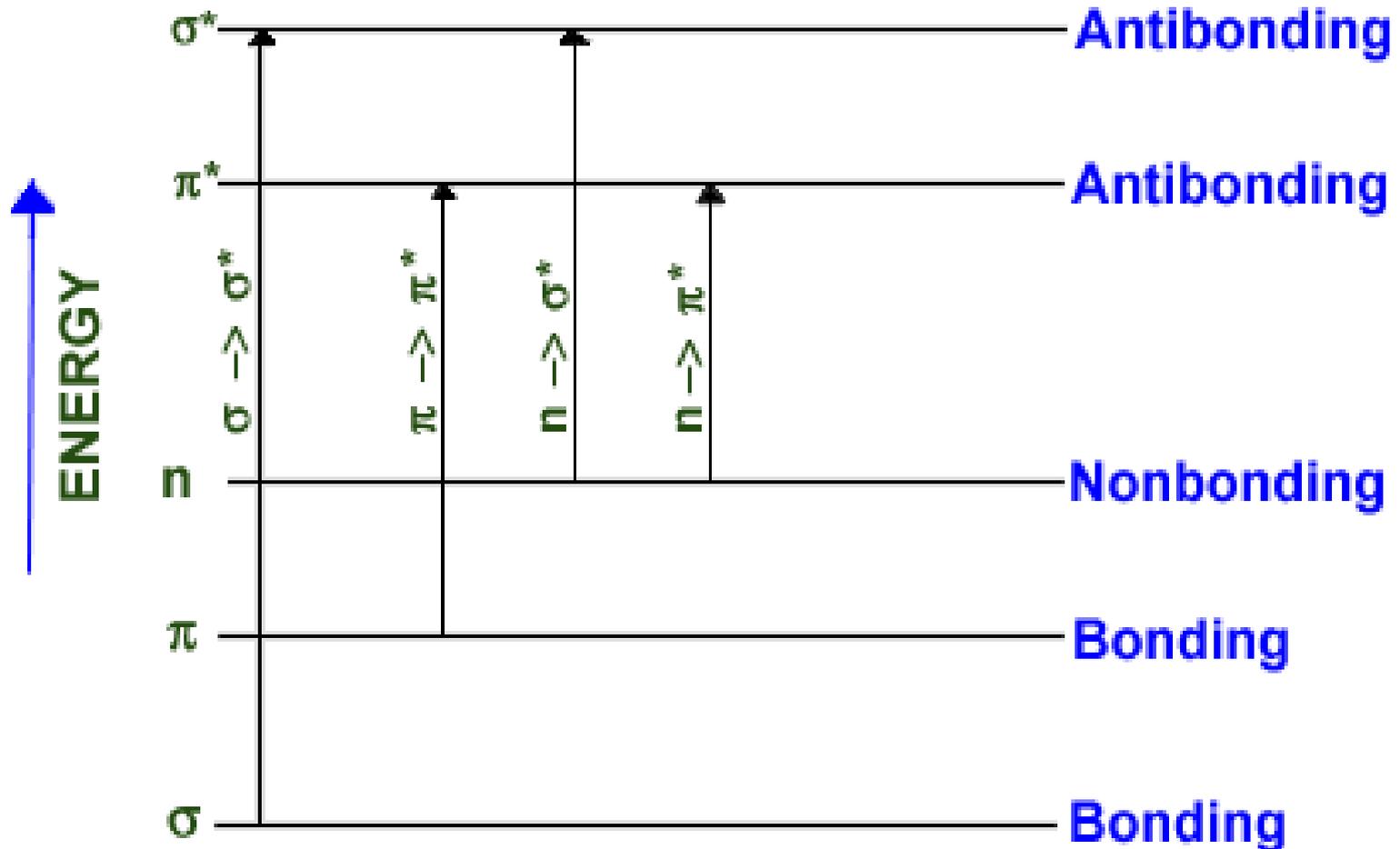


Figure: Absorption and intensity shifts

Electronic transition

- ▣ The absorption of UV or visible radiation corresponds to the excitation of outer electrons. There are three types of electronic transition which can be considered;
- ▣ Transitions involving p , s , and n electrons.
- ▣ Transitions involving charge-transfer electrons.
- ▣ Transitions involving d and f electrons .
- ▣ When an atom or molecule absorbs energy, electrons are promoted from their ground state to an excited state. In a molecule, the atoms can rotate and vibrate with respect to each other. These vibrations and rotations also have discrete energy levels, which can be considered as being packed on top of each electronic level.

Transition



Types of transition

□ σ - σ^* Transitions

- An electron in a bonding σ orbital is excited to the corresponding antibonding orbital. The energy required is large. For example, methane (which has only C-H bonds, and can only undergo σ - σ^* transitions) shows an absorbance maximum at 125 nm. Absorption maxima due to σ - σ^* transitions are not seen in typical UV-Vis. spectra (200 - 700 nm).

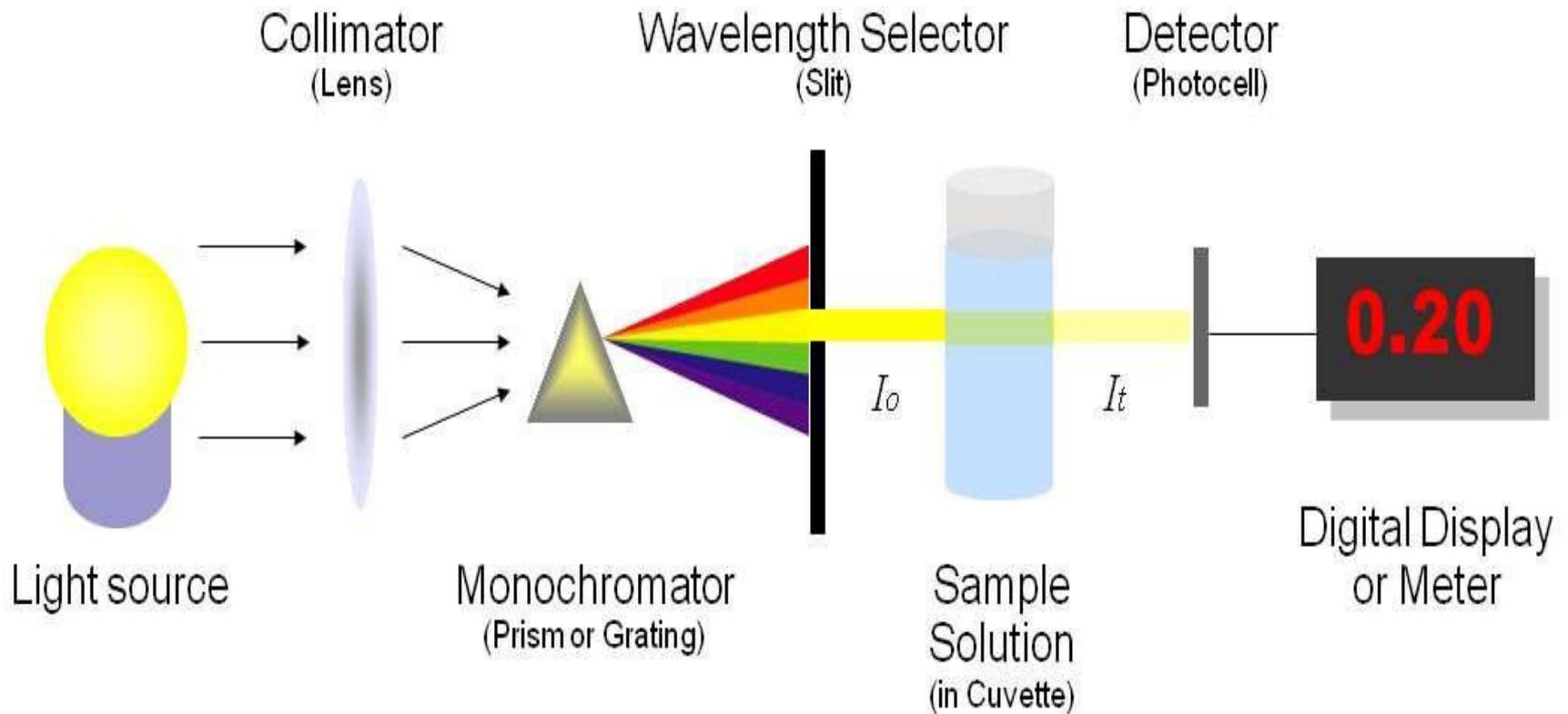
□ n - σ^* Transitions

- Saturated compounds containing atoms with lone pairs (non-bonding electrons) are capable of n - σ^* transitions. These transitions usually need less energy than σ - σ^* transitions. They can be initiated by light whose wavelength is in the range 150 - 250 nm. The number of organic functional groups with n - σ^* peaks in the UV region.

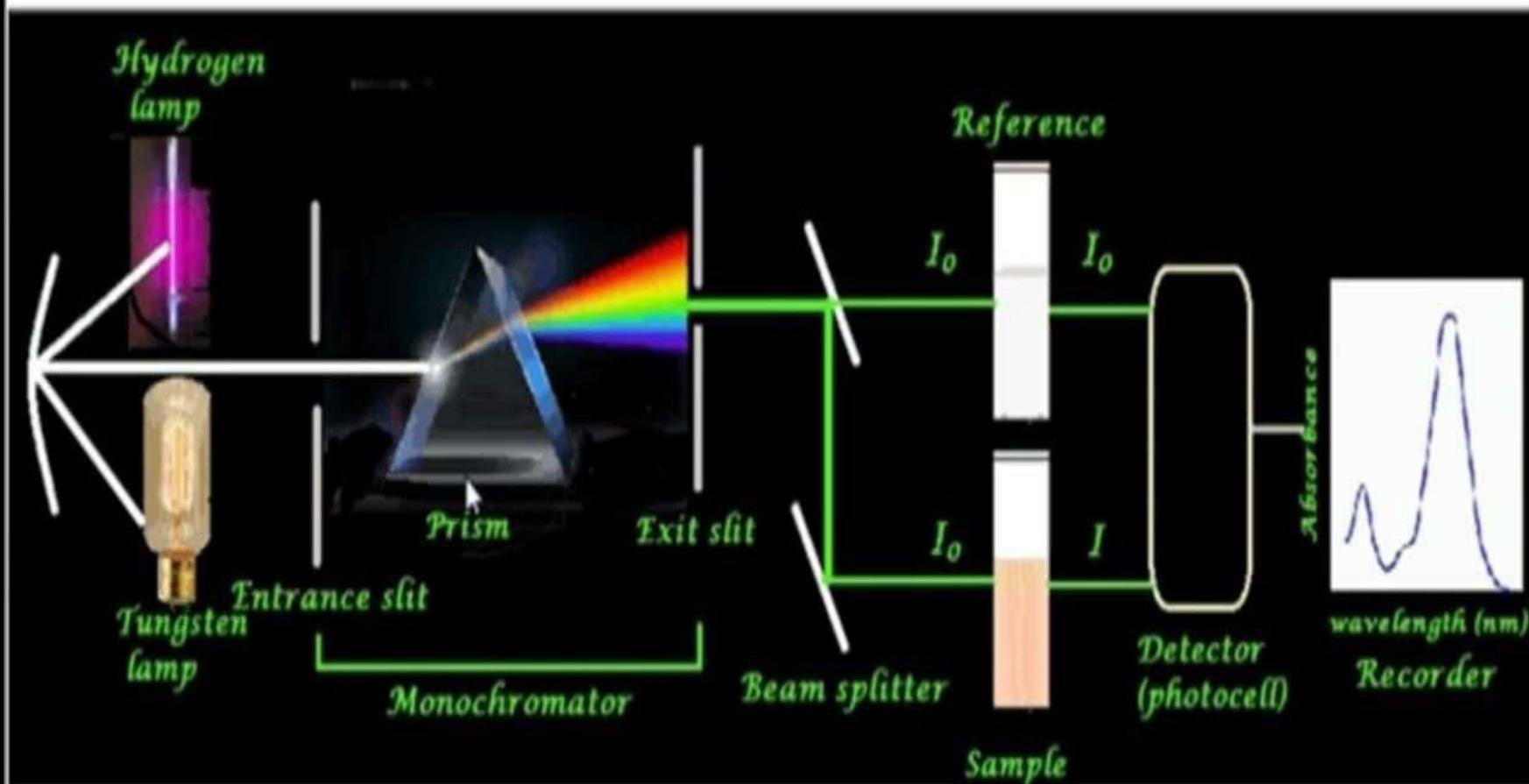
Types of transition

- ▣ ***n* - π^* and π - π^* Transitions**
- ▣ Most absorption spectroscopy of organic compounds is based on transitions of *n* or π electrons to the π^* excited state. This is because the absorption peaks for these transitions fall in an experimentally convenient region of the spectrum (200 - 700 nm). These transitions need an unsaturated group in the molecule to provide the p electrons.

Instrumentation



UV-VISIBLE SPECTROSCOPY: INSTRUMENTATION



Light source

- ▣ Tungsten filament lamps and hydrogen-deuterium lamps are most widely used and suitable light source as they cover the whole UV region
- ▣ Tungsten filament lamps are rich in red radiations; more specifically they emit the radiations of 375nm, while the intensity of hydrogen-deuterium lamps falls below 375nm.

Monochromator

- ▣ Monochromators generally is composed of prisms and slits.
- ▣ Most of the spectrophotometers are double beam spectrometer.
- ▣ The radiation emitted from the primary source is dispersed with help of rotating prisms.
- ▣ The various wavelengths of the light source which are separated by the prism are then selected by the slits such the radiation of the prism results in a series of continuously increasing wavelength to pass through the slits for recording purpose.
- ▣ The beam selected by the slits monochromatic and further divided into two beams with the help of another prism.

Sample & reference cells

- ▣ One of the two divided beams is passed through the sample solution and second beams passed through the reference solution.
- ▣ Both sample and reference solution are contained in the cells.
- ▣ These cells are made of either silica or quartz.
- ▣ Glass can not be used for the cells as it also absorbs light in the UV region.

Detector

- Generally two photocells serve the purpose of detector in UV spectroscopy.
- One of the photocell receives the beam from sample cell and second detector receives the beam from the reference.
- The intensity of the radiation from the reference cell is stronger than the beam of sample cell. This results in the generation of pulsing or alternating currents in the photocells.

Amplifier

- ▣ The alternating current generated in the photocells is transferred to the amplifier.
- ▣ The amplifier is coupled to a small servo meter.
- ▣ Generally current generated in the photocells is of very low intensity, the main purpose of amplifier is to amplify the signals many times so we can get clear and recordable signals.

RECORDING DEVICES

- ▣ Most of the time amplifier is coupled to a pen recorder which is connected to the computer.
- ▣ Computer stores all the data generated and produces the spectrum of the desired compound

Application of UV

Detection of Impurities

- It is one of the best methods for determination of impurities in organic molecules.
- Additional peaks can be observed due to impurities in the sample and it can be compared with that of standard raw material.
- By also measuring the absorbance at specific wavelength, the impurities can be detected

Structure elucidation of organic compounds

- It is useful in the structure elucidation of organic molecules, such as in detecting the presence of hetero atoms.

- ▣ UV absorption spectroscopy can be used for the quantitative determination of compounds that absorb UV radiation.
- ▣ UV absorption spectroscopy can characterize those types of compounds which absorb UV radiation thus used in qualitative determination of compounds.
- ▣ Identification is done by comparing the absorbing spectrum with the spectra of known compounds.
- ▣ This technique is used to detect the presence or absence of functional group in the group. absence of a bond at particular wavelength regarded as an evidence for absence of particular group.

- ▣ Kinetics of reaction can also be studied using uv spectroscopy. The UV radiation is passed through the reaction cell and the absorbance changes can be observed.
- ▣ Many drugs are either in the form of raw material or in the form of formulation. They can be assayed by making a suitable solution of the drug in a solvent and measuring the absorbance at specific wavelength.
- ▣ Molecular weights of compounds can be measured spectrophotometrically by preparing the suitable derivatives of these compounds.
- ▣ Uv spectrophotometer may be used as a detector for HPLC.

Advantages

- ▣ High accuracy
- ▣ Easy to handling
- ▣ Provide robust operation
- ▣ Utilized in qualitative and quantitative analysis
- ▣ Derivative graph can be obtained.
- ▣ Cost effective instrument.

Disadvantages

- ❑ Only those molecules are analyzed which have chromophores.
- ❑ Only liquid samples are possible to analyzed.
- ❑ Result of the absorption can be effective by pH ,temperature and impurities.
- ❑ It takes time to get ready to use it.
- ❑ Cuvette handling can affect the reading of the sample.

THANKS

Department of Chemistry

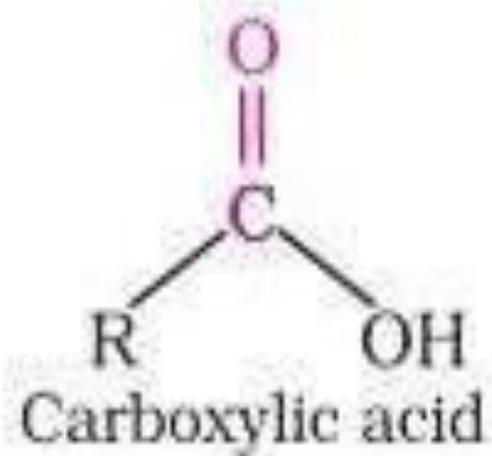
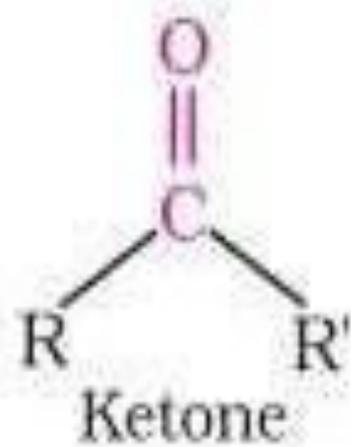
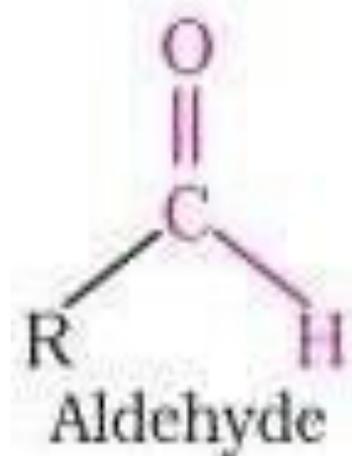
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Topic:-ALDEHYDES AND KETONES AND CARBOXYLIC ACIDS

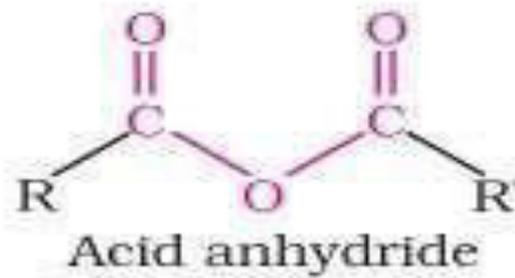
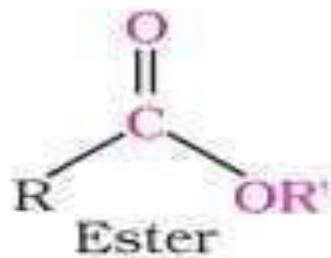
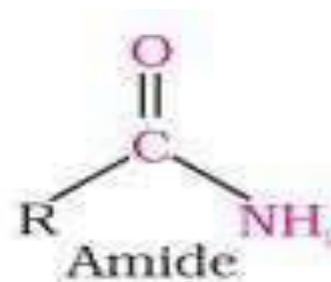
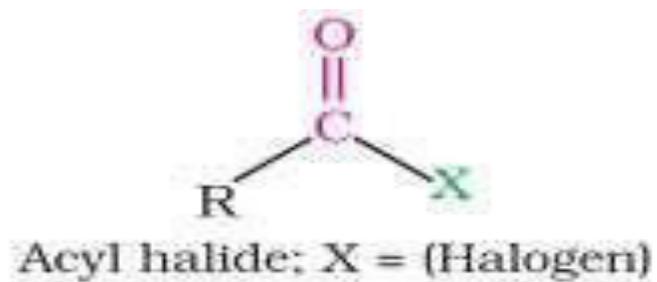
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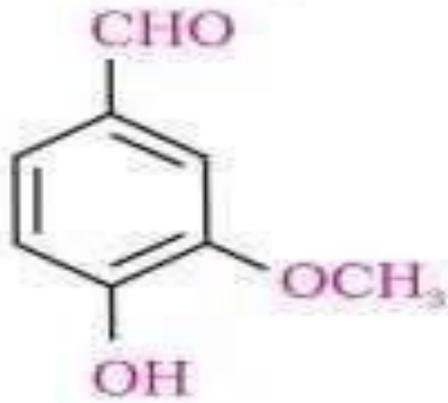
Dr.Sudhanshu dhar Dwivedi

**Aldehydes,
Ketones
and
Carboxylic acid**

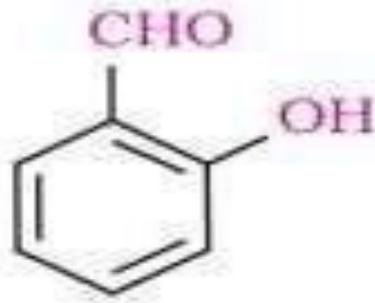


Derivatives of Carboxylic Acid

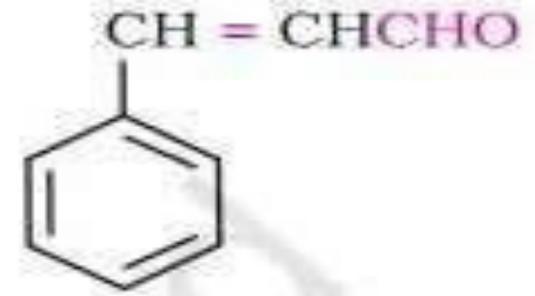




Vanillin



Salicylaldehyde



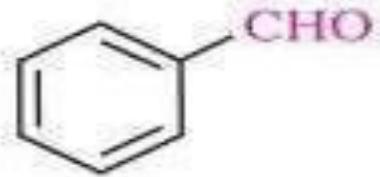
Cinnamaldehyde



Common Names



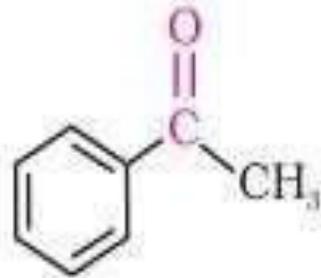
Acetaldehyde



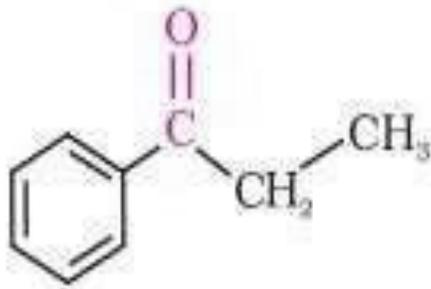
Benzaldehyde



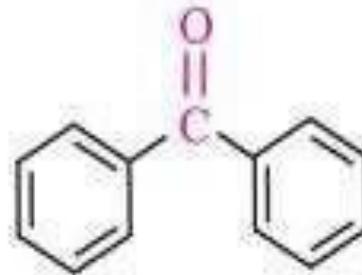
Acetone



Acetophenone

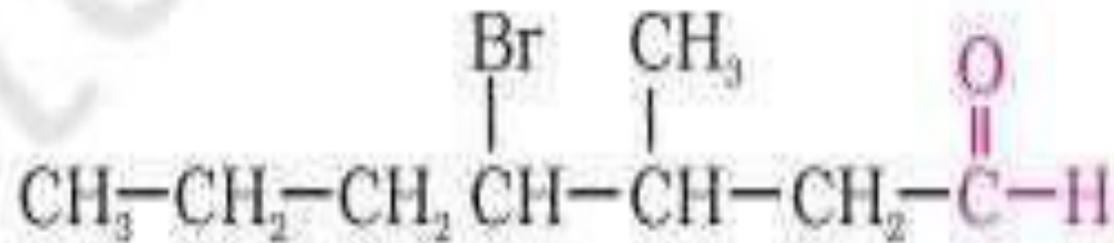
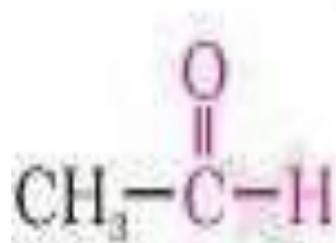


Propiophenone



Benzophenone

IUPAC Names



Structure of Carbonyl Group

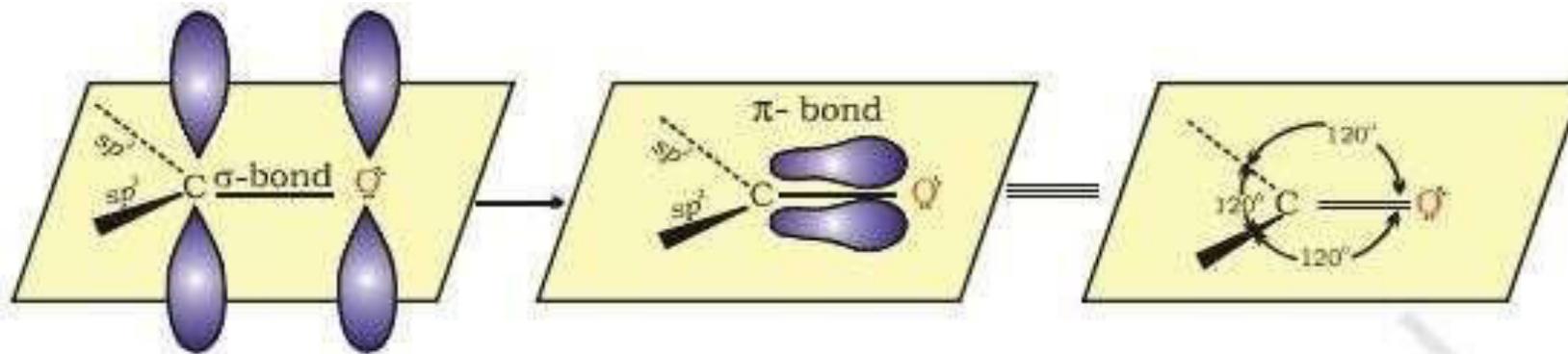
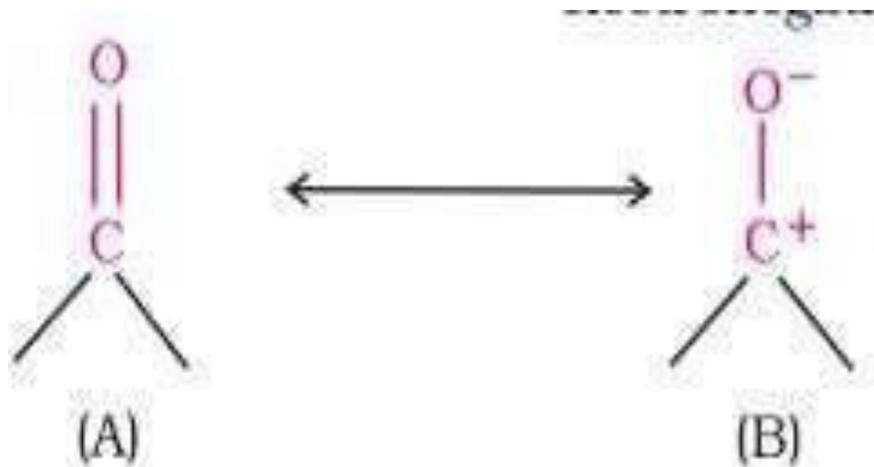


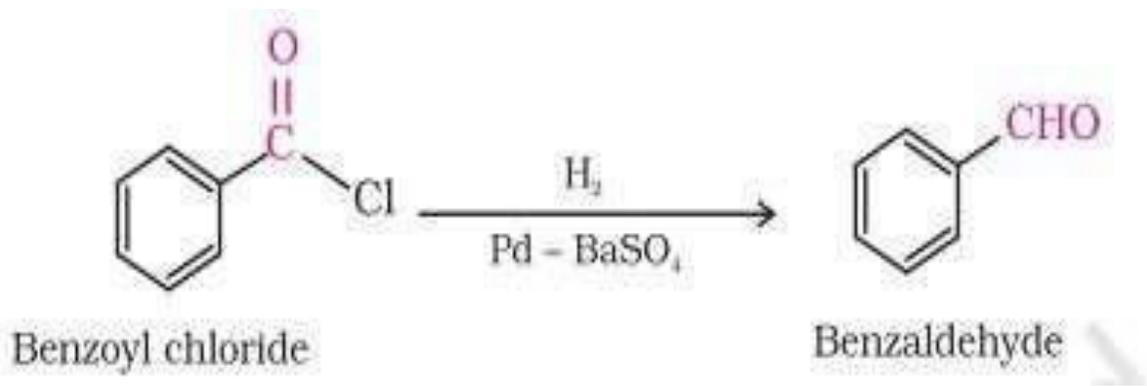
Fig.12.1 Orbital diagram for the formation of carbonyl group



- C-O bond is **polar** due to **more E.N. of Oxygen atom** as compared to C.
- Due to **+ve charge on Carbon atom**, it acts as **electrophile**.
- Due to **-ve charge on Oxygen atom**, it acts as **nucleophile**.

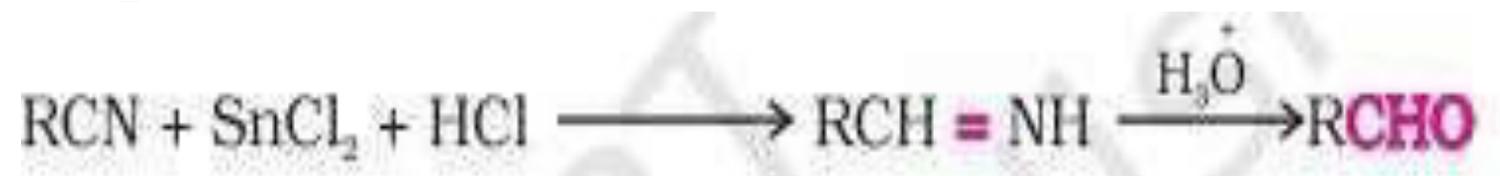
Preparation of aldehydes:

1. From acid Chlorides

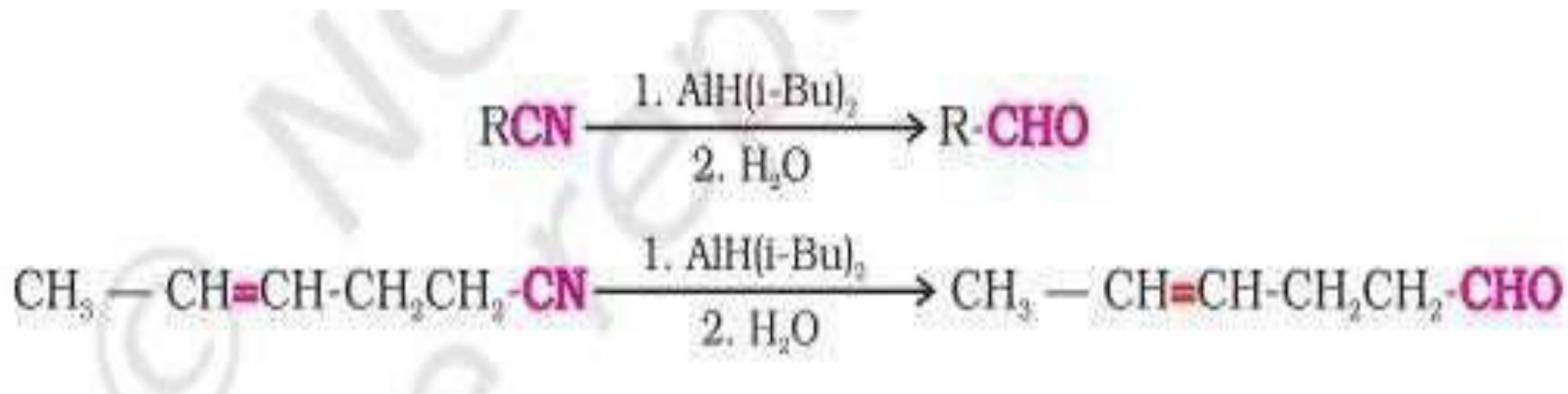


2. From nitriles and esters:

(i) Stephen reaction



- Nitriles are selectively reduced by diisobutylaluminium hydride, (DIBAL-H) to imines followed by hydrolysis to aldehydes:



- Esters are also reduced to aldehydes with DIBAL-H.

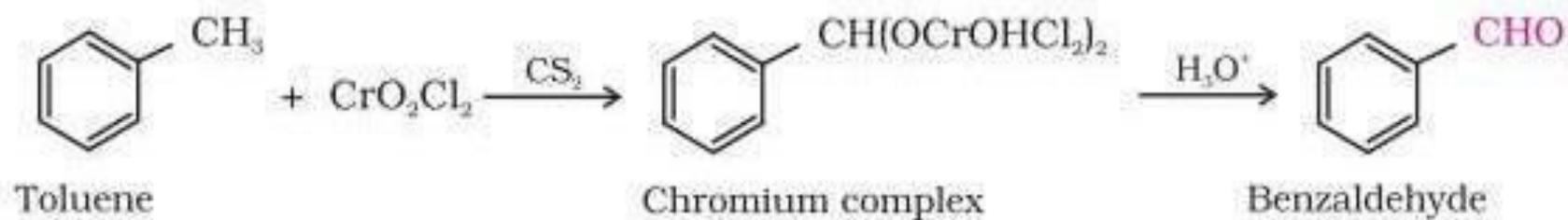


3. From hydrocarbons

Aromatic aldehydes (benzaldehyde and its derivatives) are prepared

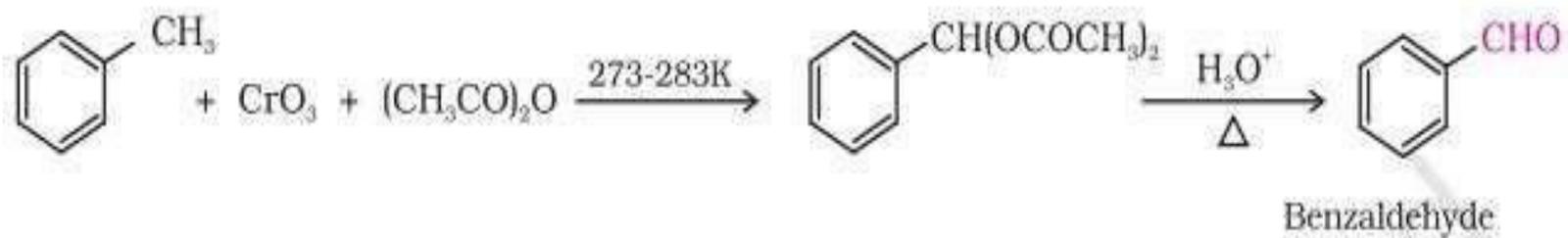
(i) *By oxidation of methylbenzene/toluene*

(a) *Use of chromyl chloride (CrO_2Cl_2):*

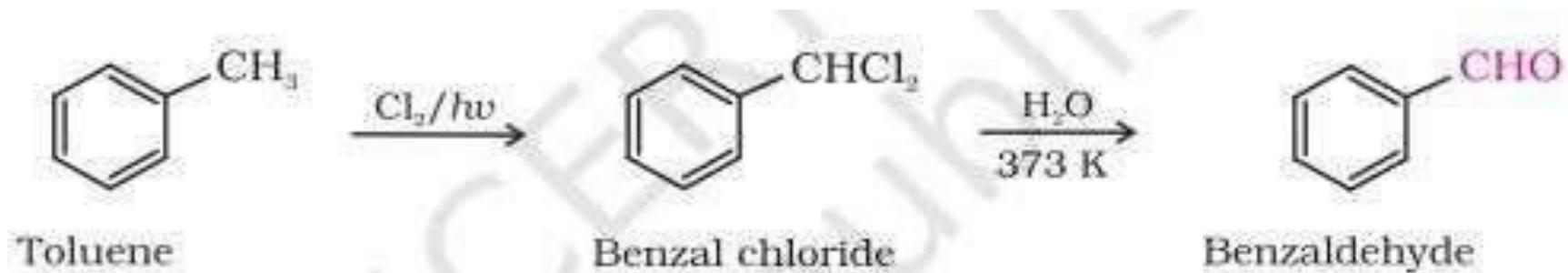


This reaction is called **Etard reaction**.

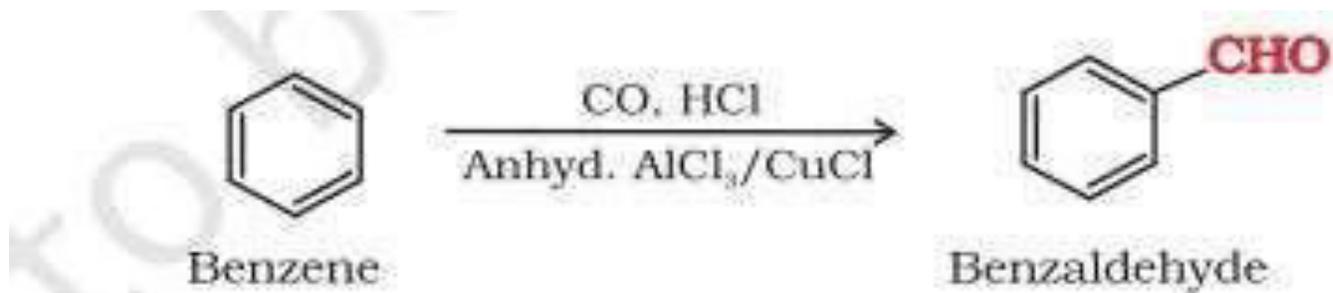
(b) Use of chromic oxide (CrO_3):



(ii) By side chain chlorination followed by hydrolysis

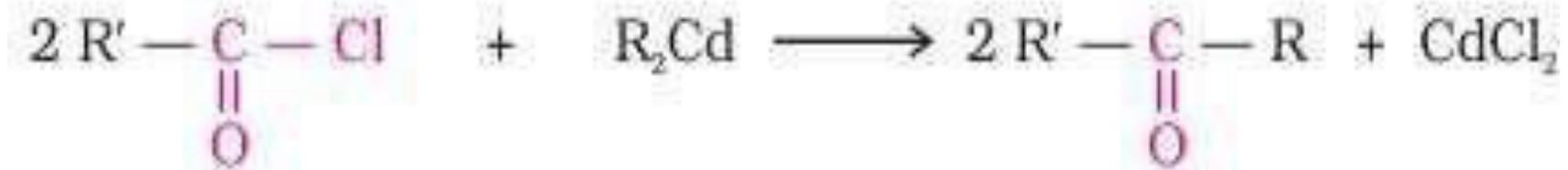
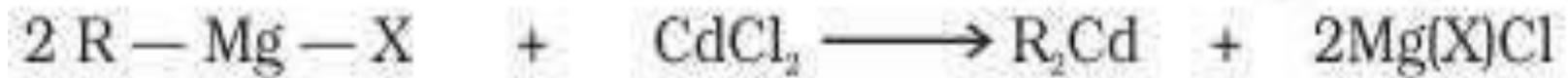


(iii) By Gattermann – Koch reaction

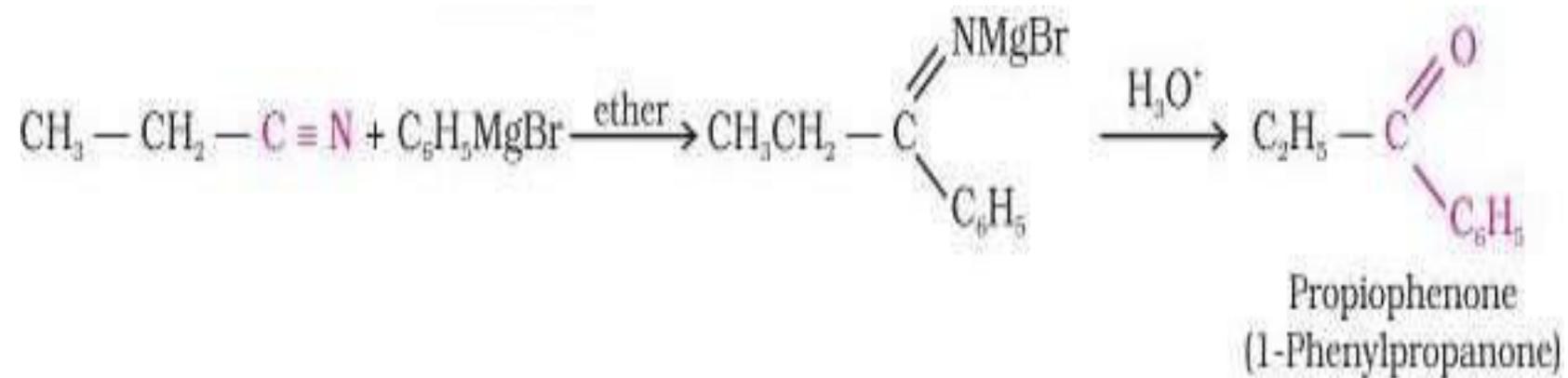


Preparation of ketones

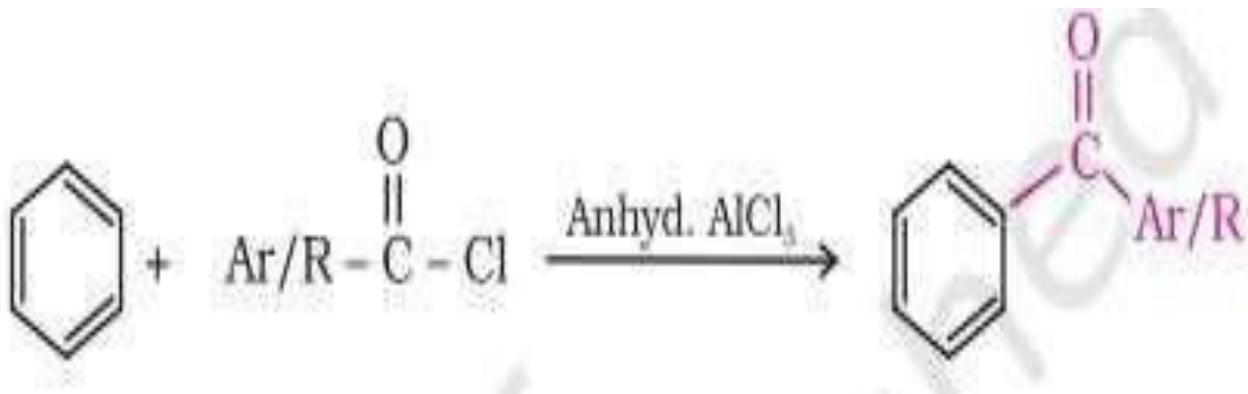
1. From acyl chlorides



2. From nitriles



3. From benzene or substituted benzenes

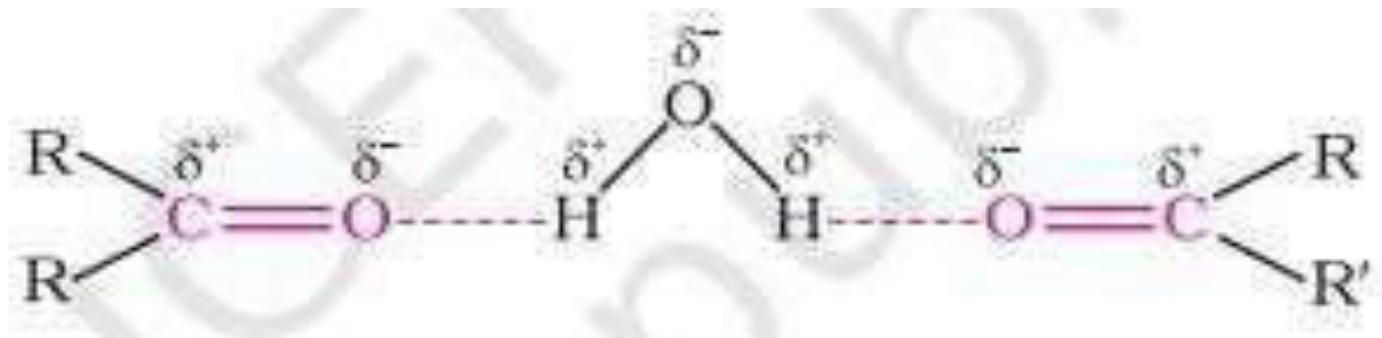


Physical Properties of Aldehydes and Ketones

1. Aldehydes and Ketones have higher boiling points than hydrocarbons, but have lower boiling points than alcohols, because they have no H attached to the O.

	b.p.(K)	Molecular Mass
n-Butane	273	58
Methoxyethane	281	60
Propanal	322	58
Acetone	329	58
Propan-1-ol	370	60

2. Small aldehydes are reasonably soluble in water. Large aldehydes are less polar and dissolve more readily in nonpolar organic solvents.



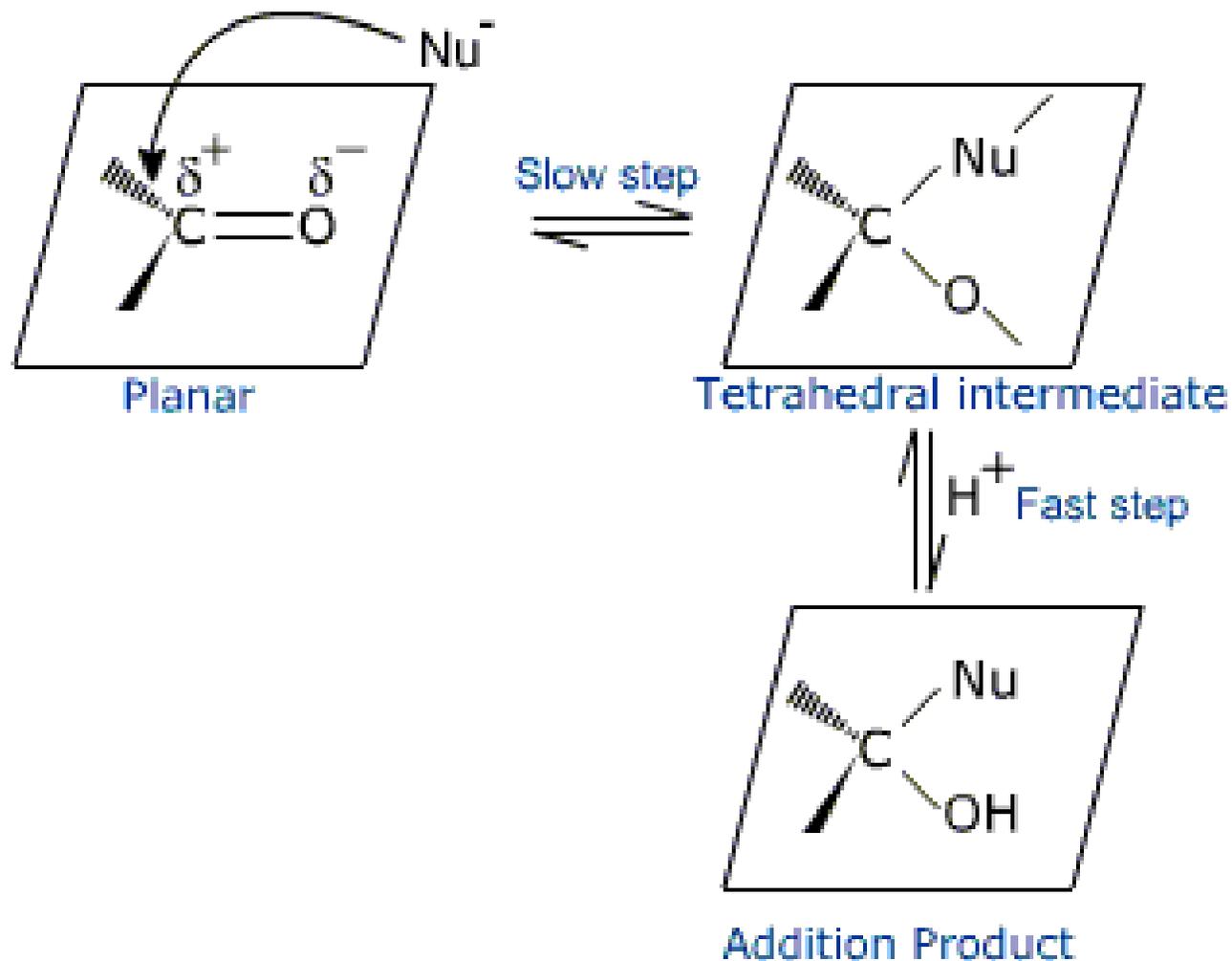
- The solubility of aldehydes and ketones decreases rapidly on increasing the length of alkyl chain.

3. Aldehydes and Ketones have strong odors, and are often used as flavorings or scents.

Chemical Reactions

1. Nucleophilic addition reactions

(i) Mechanism of nucleophilic addition reactions:

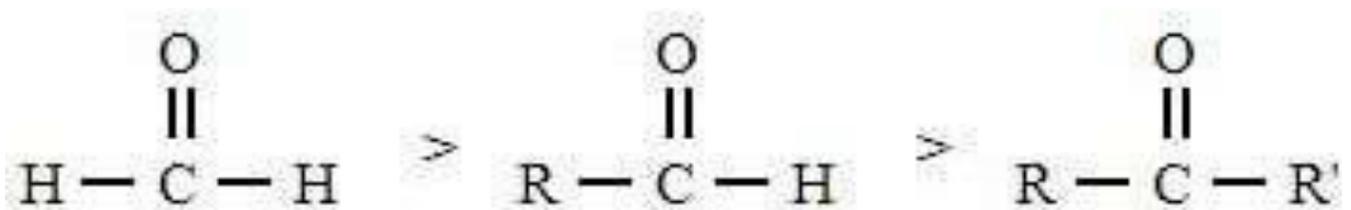


(ii) Reactivity of Aliphatic Aldehydes and Ketones:

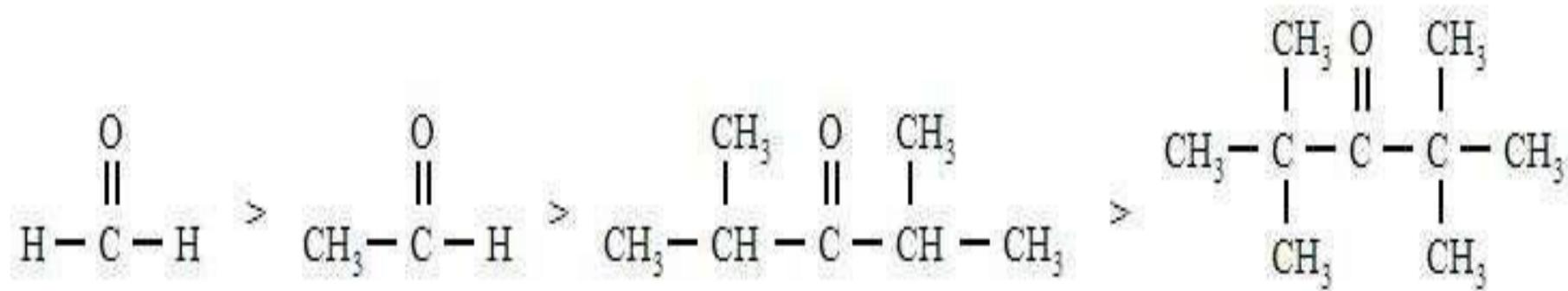
Aliphatic aldehydes are more reactive than ketones because of the following reasons :

a) Inductive effect : Alkyl groups are electron donating in nature (i.e., show +I-Effect).

Hence, the presence of alkyl groups attached to the carbonyl group increases the electron density on the carbonyl carbon thereby decreases its reactivity towards nucleophilic addition reactions. Therefore, the order of reactivity is :

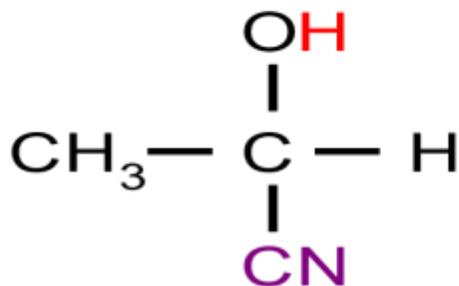
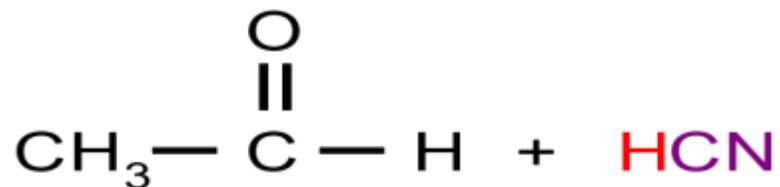


b) **Steric hinderance** : The more the number and the bigger the size of the alkyl group, the more difficult for a nucleophile to attack due to steric hinderance (crowding). Hence, the order of reactivity is :

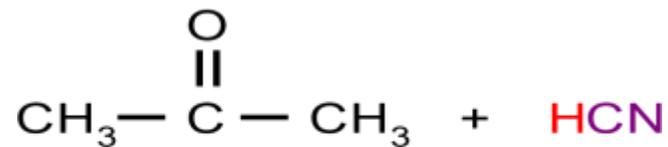


I. Addition of Hydrogen Cyanide

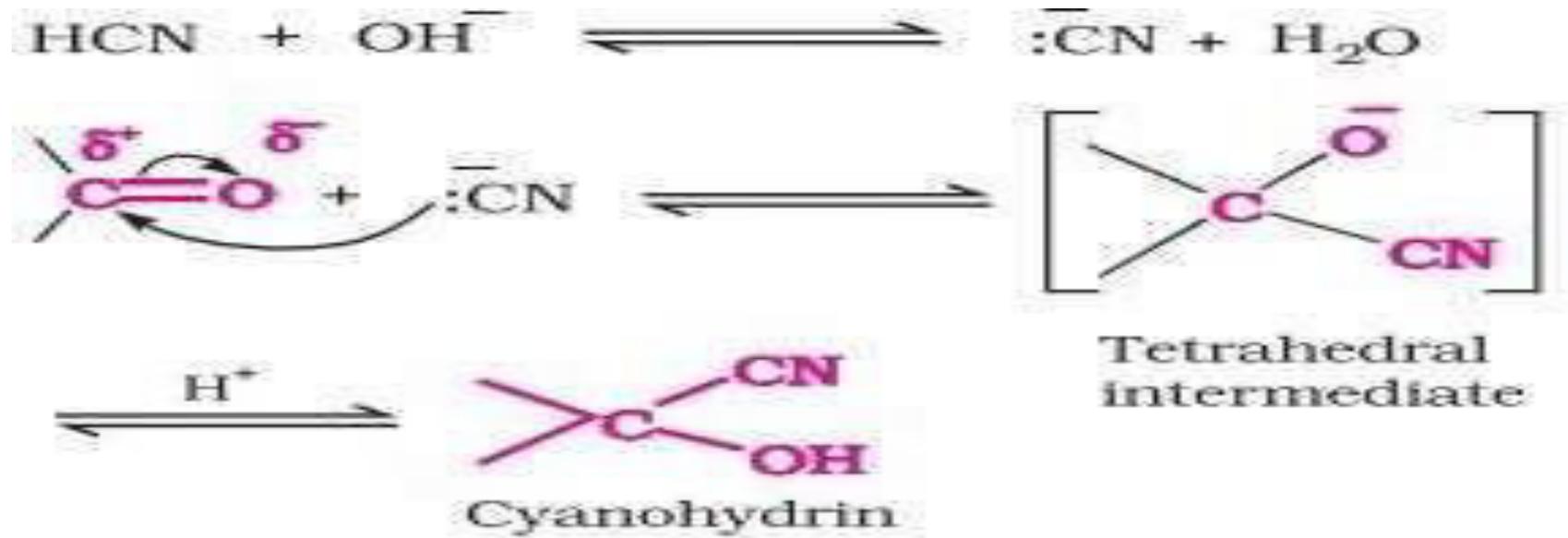
Aldehydes and ketones react with hydrogen cyanides to give cyanohydrin. The reaction of ethanal with HCN is given below.



Acetal cynohydrin

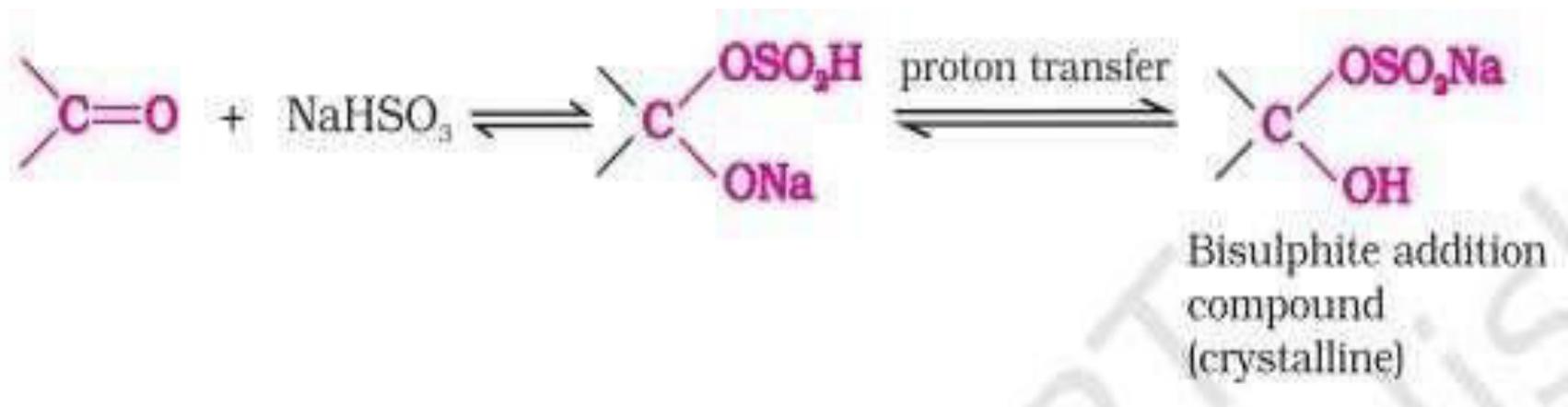


Mechanism



II. Addition of Sodium Hydrogen Sulphite

- Aldehydes react with sodium bisulphite (sodium hydrogen sulphite) to give addition products.
- Ketones, except for methyl ketones, do not react with sodium bisulphite due to steric hinderance (crowding).

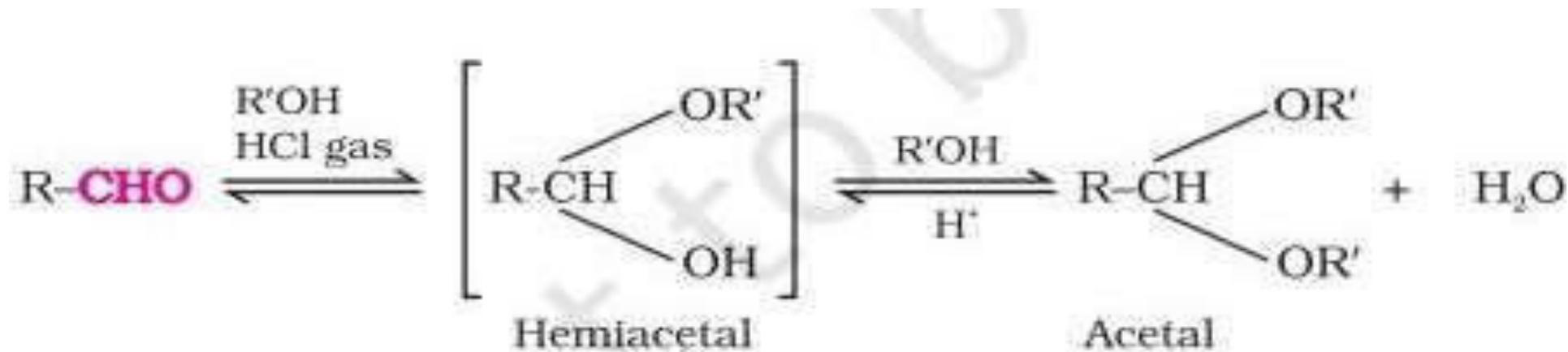


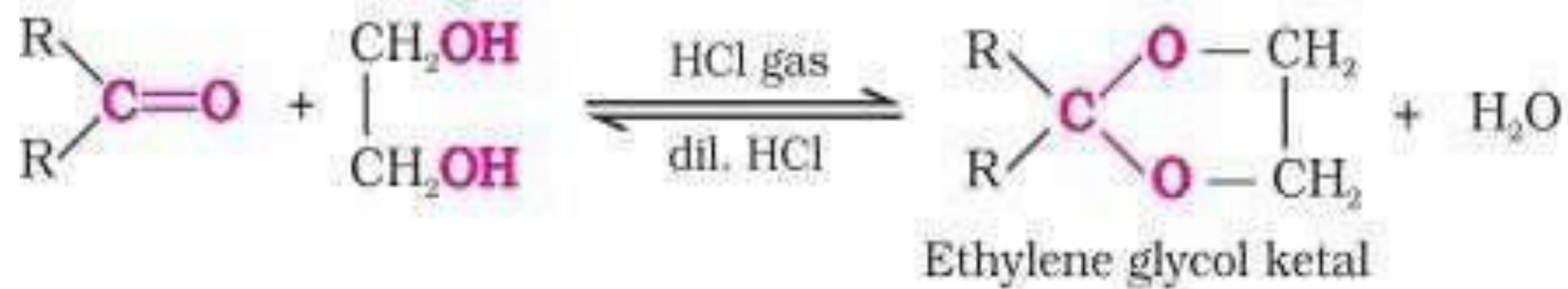
III. Addition of Grignard's Reagents to Aldehydes and Ketones

Aldehydes and ketones react with Grignard's reagents to form alcohols.

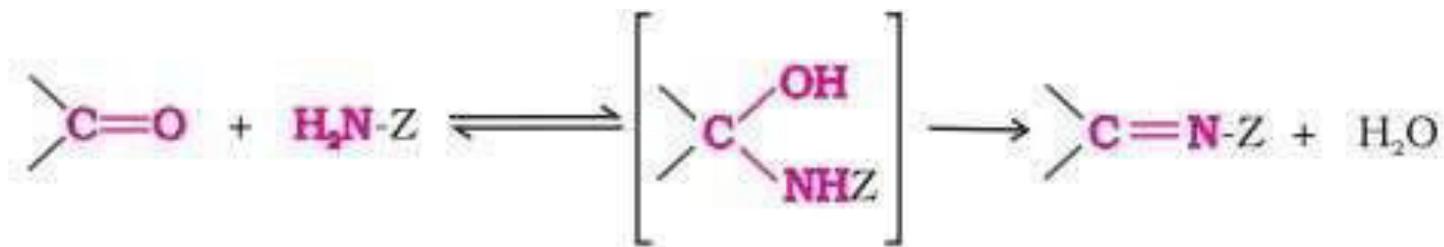
IV. Addition of Alcohols to Aldehydes and Ketones

- Aldehydes react with alcohols in the presence of dry HCl to give **hemiacetals**.
- Hemiacetals being unstable react with another molecule of alcohol to give **acetals**.





V. Addition of ammonia and its derivatives:



Z = Alkyl, aryl, OH, NH₂, C₆H₅NH, NHCONH₂, ε

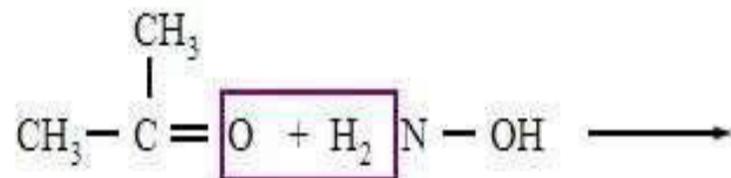
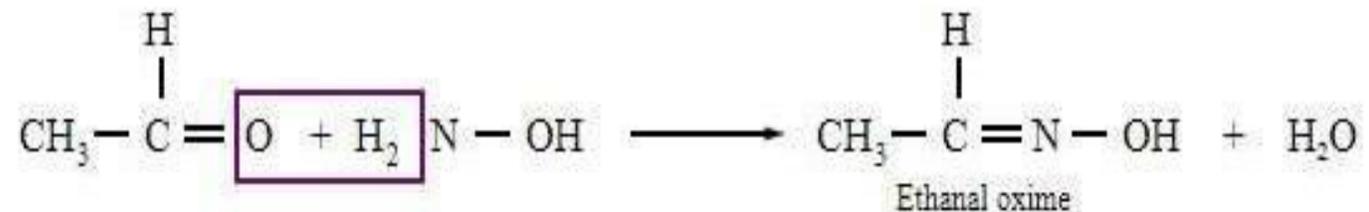
Aldehydes and ketones react with a number of ammonia derivatives in the presence of acids to form addition products.

Some ammonia derivatives are given below :

- **NH₂OH (hydroxylamine)**
- **NH₂-NH₂ (hydrazine)**
- **C₆H₅NHNH₂ (phenylhydrazine)**
- **NH₂CONH₂ (Semicarbazide)**

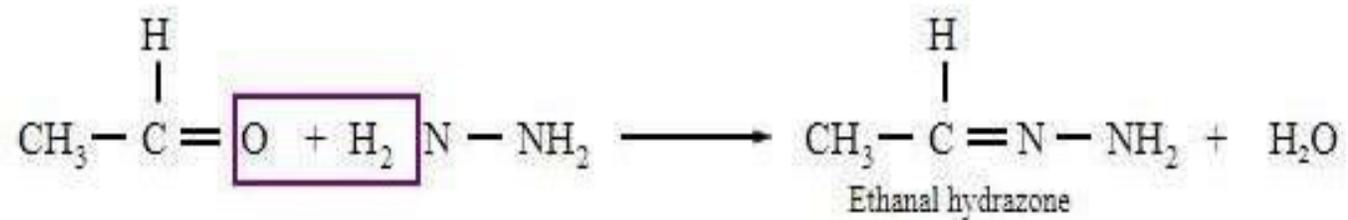
a. Reaction with Hydroxylamine

Aldehydes and ketones react with hydroxylamine (NH₂OH) to form **oximes**.



b. Reaction of Aldehydes and Ketones with Hydrazine

Aldehydes and ketones react with hydrazine (NH₂–NH₂) to form **hydrazones**.



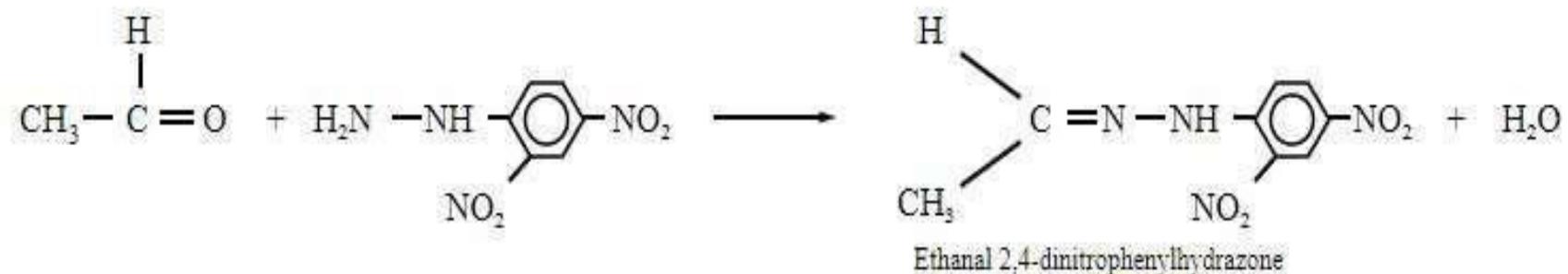
Similarly, aldehydes and ketones react with phenylhydrazines ($\text{C}_6\text{H}_5\text{NHNH}_2$) to form **phenylhydrazones**.



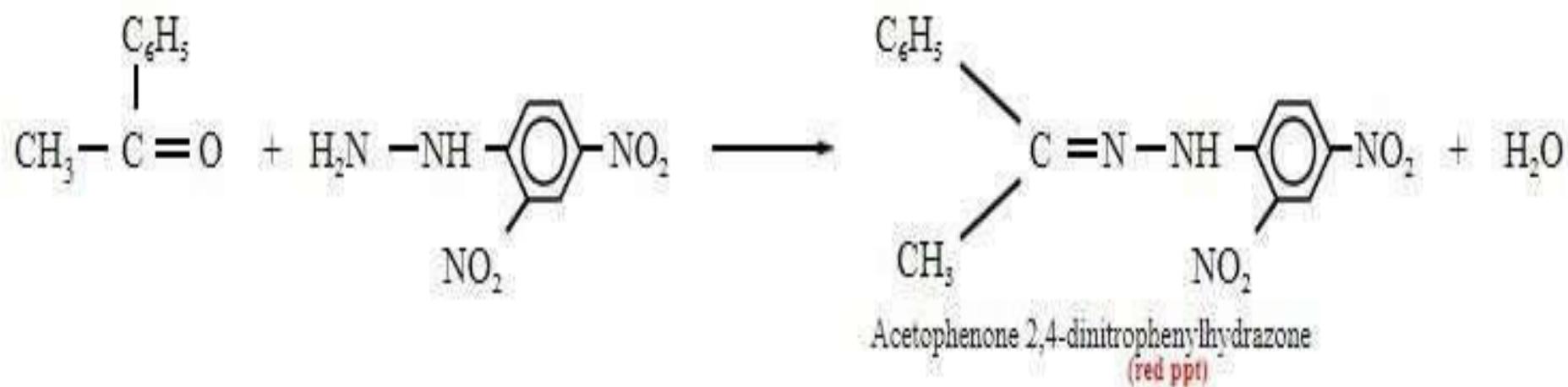
c. 2,4-DNP Test

- Aldehydes and ketones react with 2,4-dinitrophenylhydrazine to form yellow, orange or red ppt.
- This reaction is used for distinction of aldehydes and ketones from other compounds and is known as **2,4-DNP test** or **Brady's test** .

Aliphatic aldehydes and ketones give yellow ppt with 2,4-dinitrophenylhydrazine.



We get red ppt with aromatic aldehydes and ketones.



d. Reactions of Aldehydes and Ketones with semicarbazides

Aldehydes and ketones react with semicarbazide ($\text{NH}_2\text{CONHNH}_2$) to form semicarbazones.

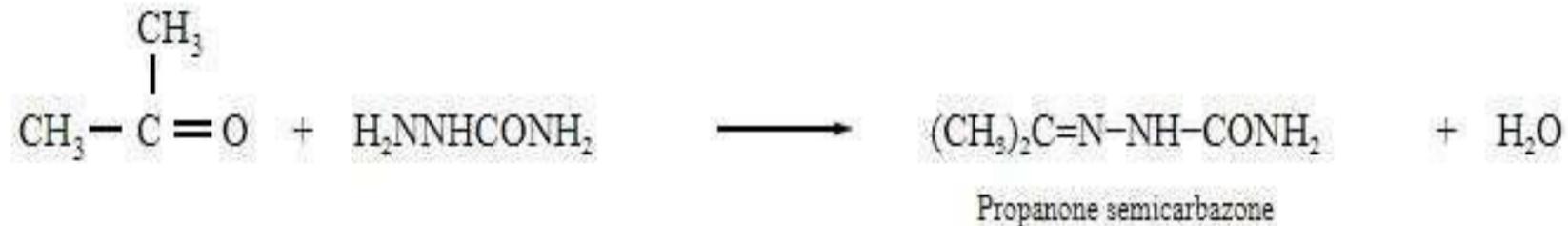
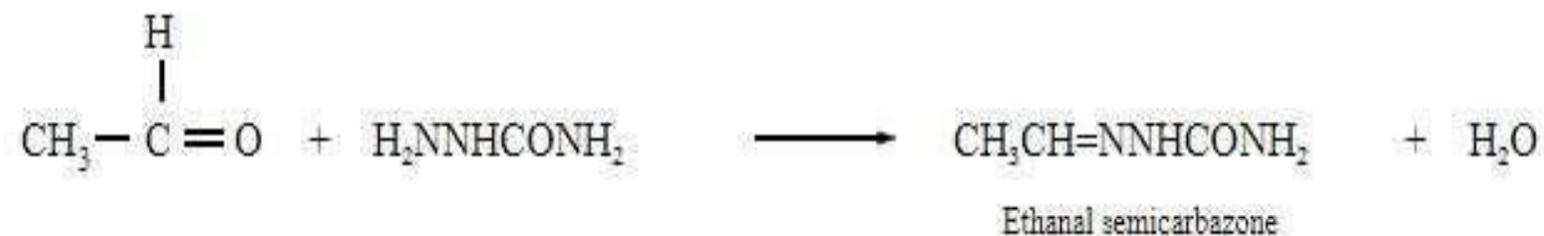
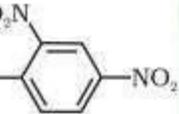


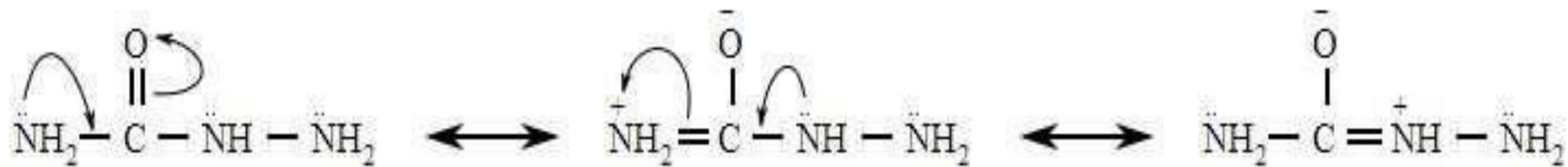
Table 12.2: Some N-Substituted Derivatives of Aldehydes and Ketones ($>C=N-Z$)

Z	Reagent name	Carbonyl derivative	Product name
-H	Ammonia	$>C=NH$	Imine
-R	Amine	$>C=NR$	Substituted imine (Schiff's base)
-OH	Hydroxylamine	$>C=N-OH$	Oxime
-NH ₂	Hydrazine	$>C=N-NH_2$	Hydrazone
-HN- 	Phenylhydrazine	$>C=N-NH-$	Phenylhydrazone
-HN- 	2,4-Dinitrophenylhydrazine	$>C=N-NH-$	2,4 Dinitrophenylhydrazone
-NH-C(=O)-NH ₂	Semicarbazide	$>C=N-NH-C(=O)-NH_2$	Semicarbazone

* 2,4-DNP-derivatives are yellow, orange or red solids, useful for characterisation of aldehydes and ketones.

Question : There are two -NH_2 groups in semicarbazide. However, only one is involved in the formation of semicarbazones. Explain why.

Answer : The lone pair on NH_2 group directly attached to the carbonyl carbon is involved in resonance.

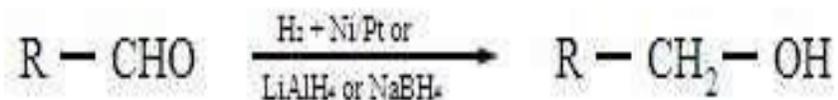


As a result, electron density of this NH_2 group decreases; therefore this NH_2 group does not act as a nucleophile. The lone pair of other NH_2 group, which is attached to NH , is not involved in resonance; hence this NH_2 group acts as a nucleophile.

2. Reduction of Aldehydes and Ketones to Alcohols

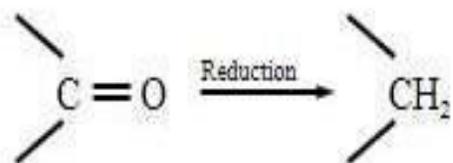
Aldehydes and ketones are reduced to primary and secondary alcohols respectively. Any one of the following reducing agents can be used for this purpose.

1. H_2 in the presence of Ni, Pt or Pd.
2. Lithium aluminium hydride ($LiAlH_4$).
3. Sodium borohydride ($NaBH_4$).



Reduction of Aldehydes and Ketones to Hydrocarbons

The carbonyl group in aldehydes and ketones can be reduced to $-CH_2$ group to form hydrocarbons.



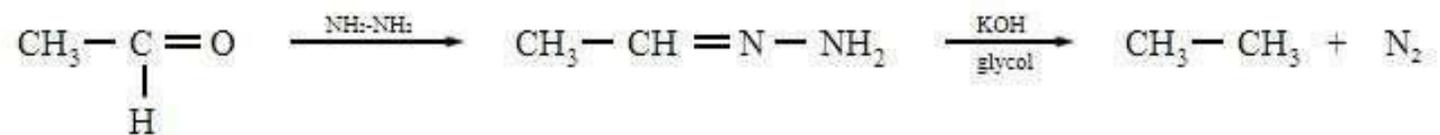
Clemmensen Reduction

Zinc amalgam (Zn-Hg) and conc. HCl are used for reduction of aldehydes and ketones to hydrocarbons. Reduction of aldehydes and ketones by this method is known as **Clemmensen reduction**.



Wolff-Kishner reduction

Alternatively, the carbonyl group can be reduced to hydrocarbon using hydrazine ($\text{NH}_2\text{-NH}_2$) followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol. Reduction by this method is known as **Wolff-Kishner reduction**.



3. Oxidation

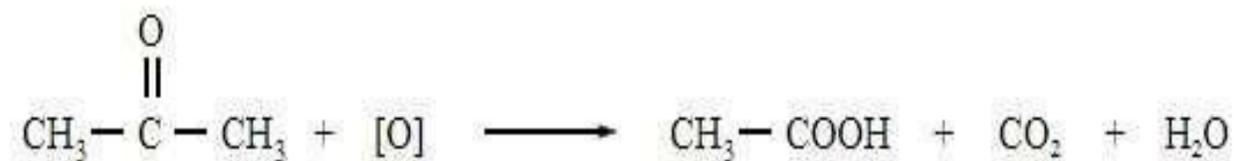
Oxidation of Aldehydes

Aldehydes are easily oxidised to carboxylic acids containing the same number of carbon atoms with oxidising agents like acid dichromate ($\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$) and KMnO_4 . The oxygen of an oxidising agent is usually represented by **[O]**.



(ii) Oxidation of Ketones

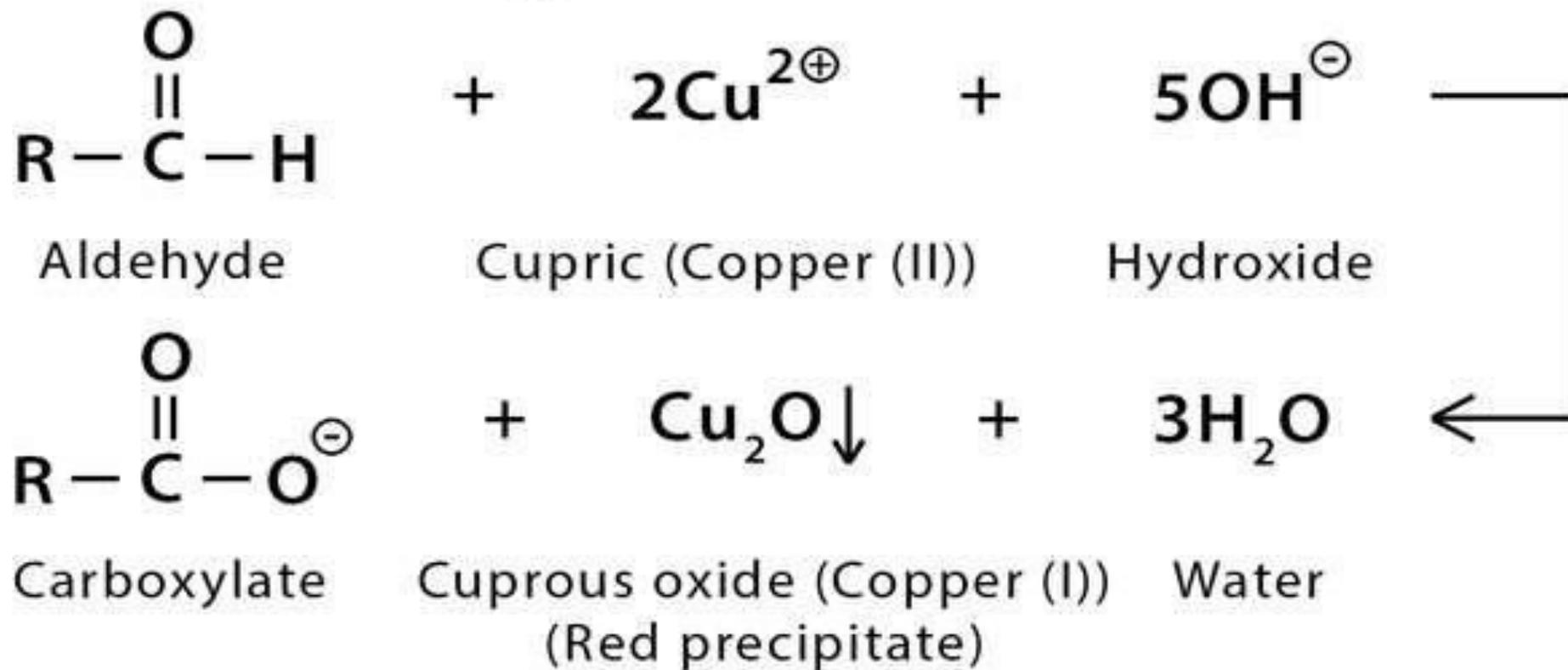
Ketones do not undergo oxidation easily and on vigorous oxidation yield acids with lesser number of carbon atoms.

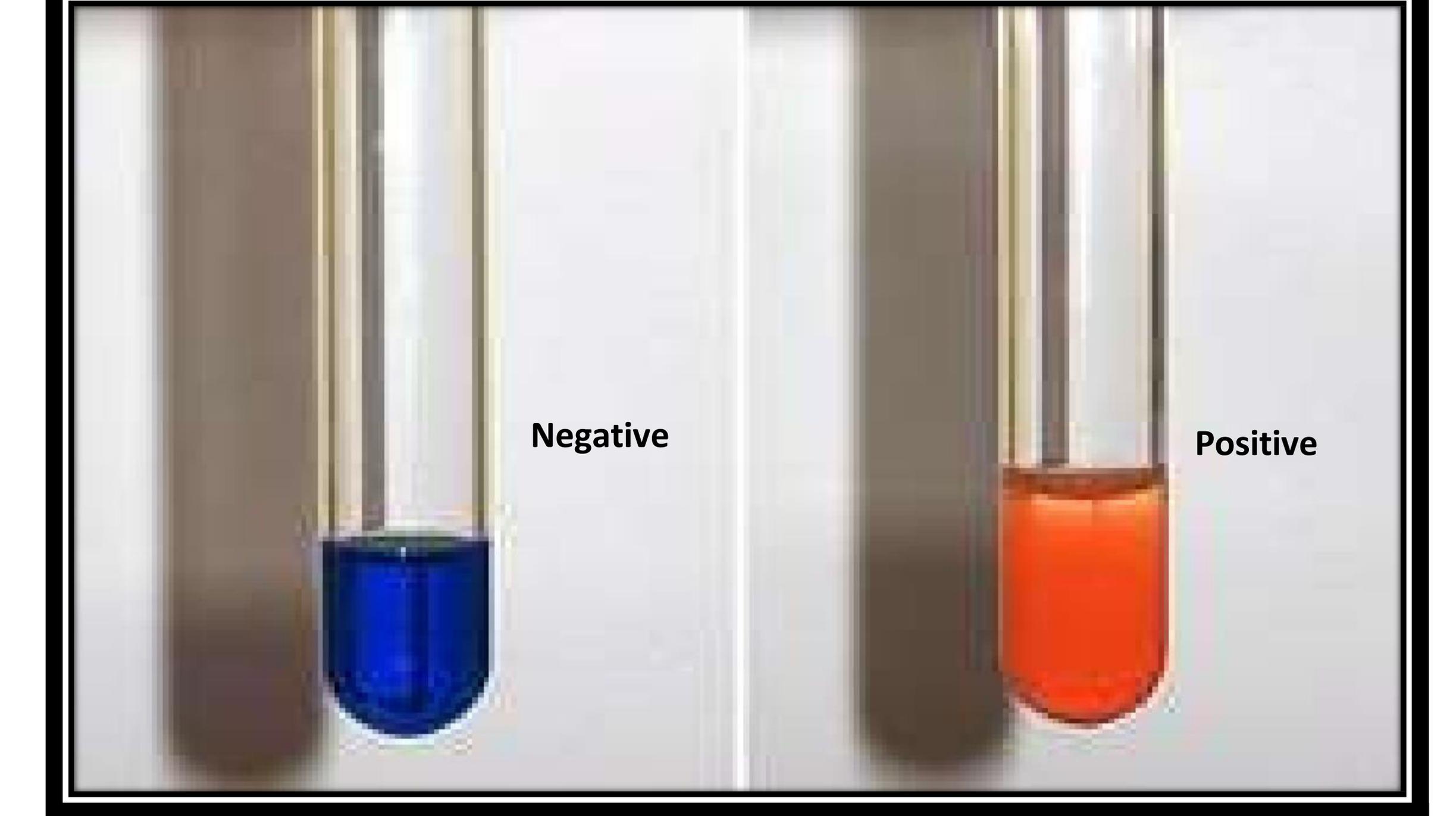




Tollen's test
Positive result (silver mirror)

(ii) Fehling's Test Reaction



The image shows two test tubes side-by-side. The left test tube contains a blue liquid and is labeled 'Negative'. The right test tube contains an orange liquid and is labeled 'Positive'. Both test tubes are held in a rack against a white background.

Negative

Positive

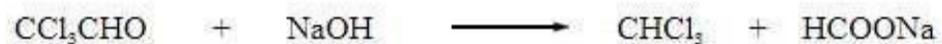
Tests to Distinguish Aldehydes and Ketones, and Aliphatic Aldehydes and Aromatic Aldehydes

TESTS	ALDEHYDES	KETONES
<p><i>Tollens' Test / silver mirror test</i> Reagent and condition: - ammoniacal silver nitrate solution ($[\text{Ag}(\text{NH}_3)_2]^+$)</p>	<p>Observation: Formation of silver mirror</p>	<p>Observation: Silver mirror did not formed * Ketones do not react with Tollens' reagent</p>
<p><i>Fehling's test / Benedict's test</i> Reagent and condition: - Solution of Cu^{2+} (aq) ions in an alkaline solution of sodium potassium tartate.</p> <p>* Can be used to distinguish between:</p> <ol style="list-style-type: none">Aldehydes and ketonesAliphatic aldehydes and benzaldehyde	<p>Observation; Blue colour of the Fehling's solution disappears and brick-red precipitate is obtained</p> <p>* <i>Except benzaldehyde</i></p>	<p>Observation: Blue colour remains. * Ketones do not react with Fehling's/Benedict's reagent</p>

(iii) Oxidation of methyl ketones by haloform reaction:

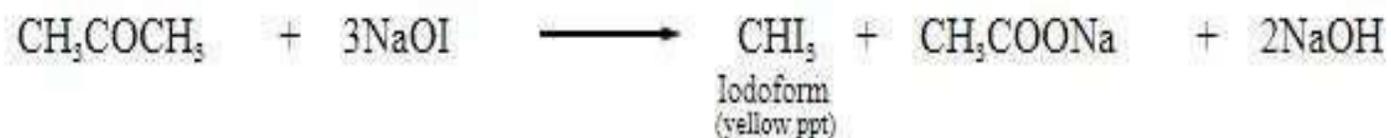
Haloform reaction

Aldehydes and ketones having methyl group attached to $>C=O$ are oxidised by sodium hypohalite ($NaOX$ or X_2+NaOH) to haloforms.



Iodoform test

When sodium hypoiodide (NaOI or I₂/NaOH) is used in the above haloform reaction, yellow ppt of iodoform is formed. Due to this reason, this reaction is used for detection of CH₃CO group – or CH₃CH(OH) which is discussed in distinction between alcohols.



Question : Give simple chemical tests to distinguish between the following pairs of compounds:

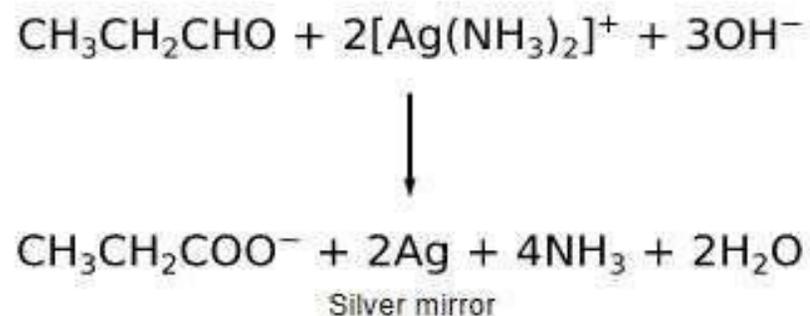
1. *Propanal and propanone*
2. *Acetophenone and benzophenone*
3. *Pentan-2-one and pentan-3-one*
4. *Benzaldehyde and acetophenone*
5. *Ethanal and propanal*

Answer :

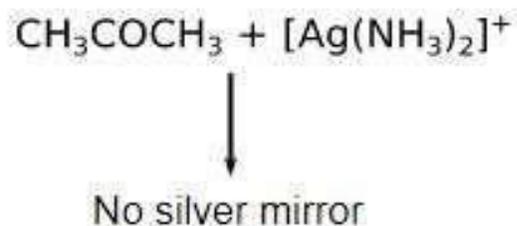
1. Propanal (CH₃CH₂CHO) and Propanone (CH₃COCH₃)

- **Tollen's test:** Propanal being an aldehyde gives Tollen's test but propanone, which is a ketone, does not.

Reaction of propanal with Tollen's reagent:

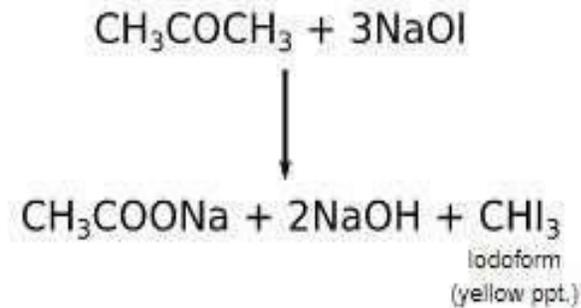


Propanone being a ketone does not give Tollen's test:

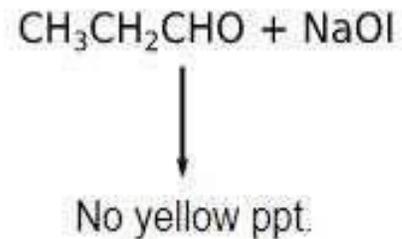


- **Iodoform test:** Since propanone is a methyl ketone, it gives yellow ppt. with iodoform. Propanal does not give this test.

Propanone gives iodoform test.



Propanal does not give iodoform test



2. Acetophenone ($C_6H_5COCH_3$) and Benzophenone ($C_6H_5COC_6H_5$)

- **Iodoform test:** Acetophenone is a methyl ketone; therefore, it gives positive iodoform test. Benzophenone is not a methyl ketone; hence, does not give this test.

3. Pentan-2-one ($CH_3COCH_2CH_2CH_3$) and Pentan-3-one ($CH_3CH_2COCH_2CH_3$)

- **Iodoform test:** Pentan-2-one being a methyl ketone gives iodoform test. Pentan-3-one does not give this test.

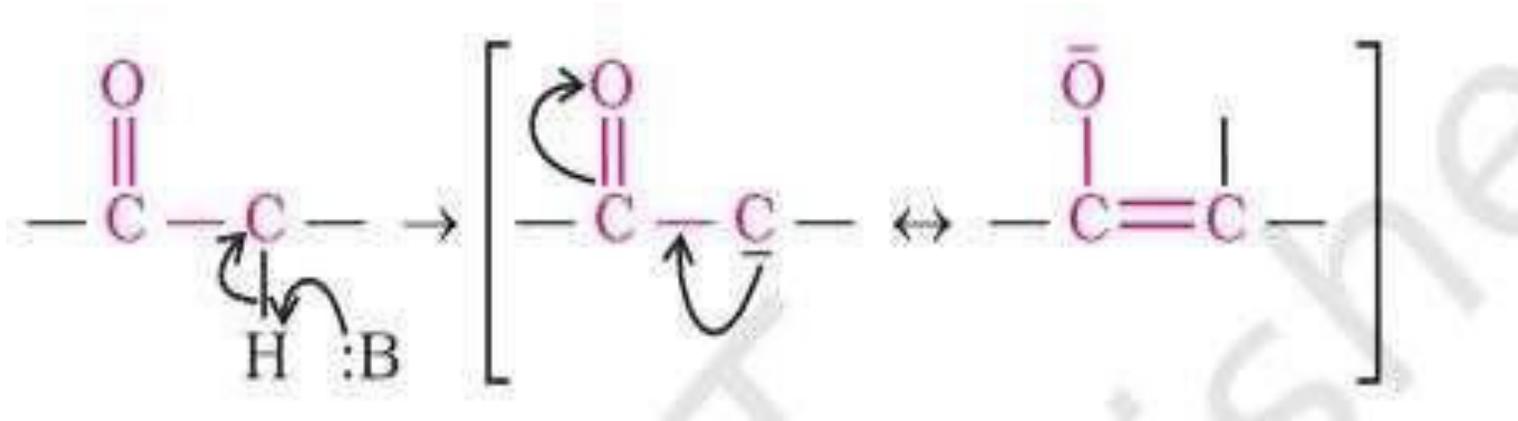
4. Benzaldehyde and acetophenone

- **Tollen's test:** Benzaldehyde is an aldehyde; hence, it reduces Tollen's reagents. Acetophenone being a ketone does not.
- **Iodoform test:** Acetophenone gives iodoform test because it is a methyl ketone. Benzaldehyde does not give this test.

Ethanal (CH_3CHO) and propanal (CH_3CH_2CHO)

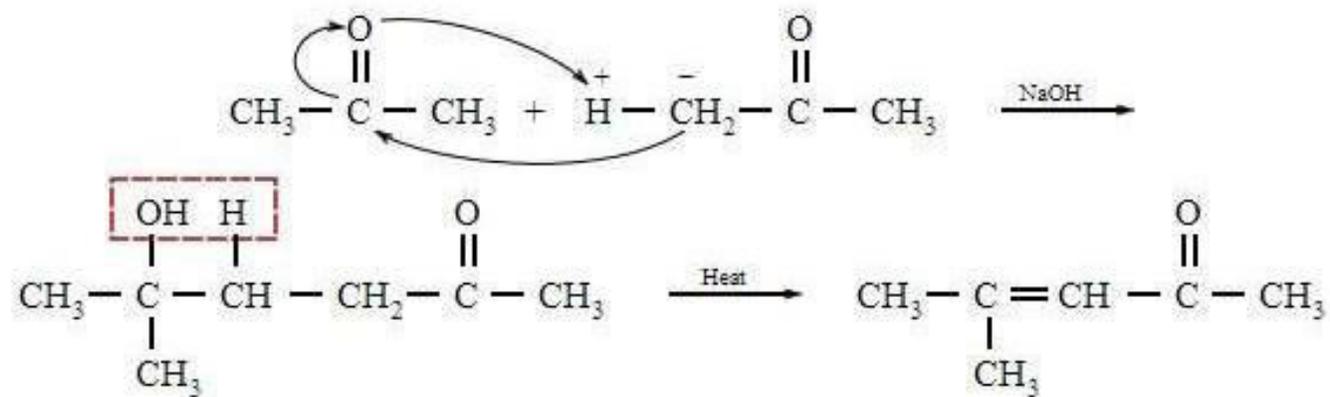
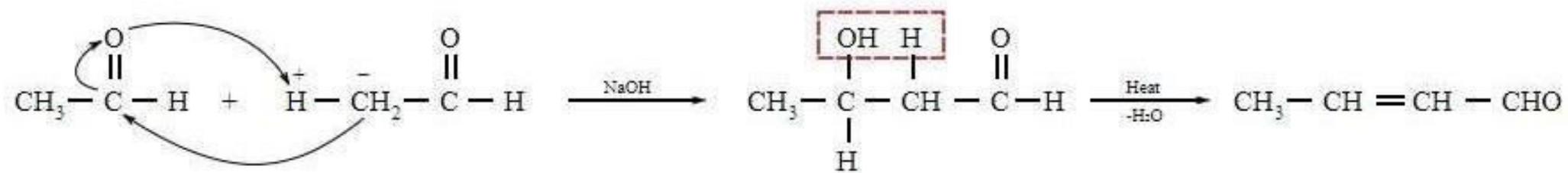
- **Iodoform test:** Ethanal gives iodoform test whereas propanal does not (why?).

4. Reactions due to α -hydrogen



Aldol condensation

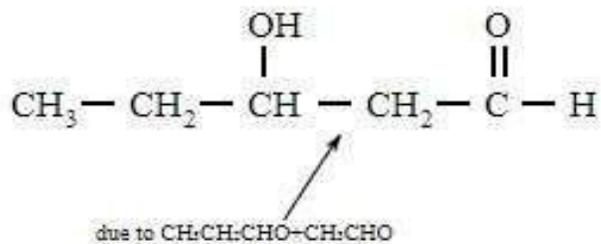
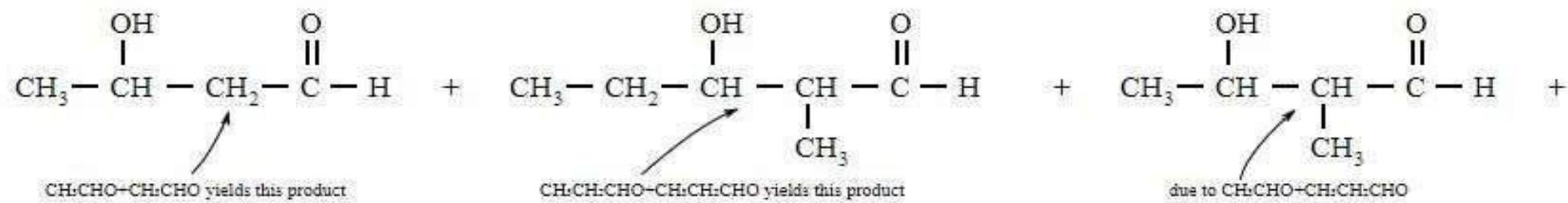
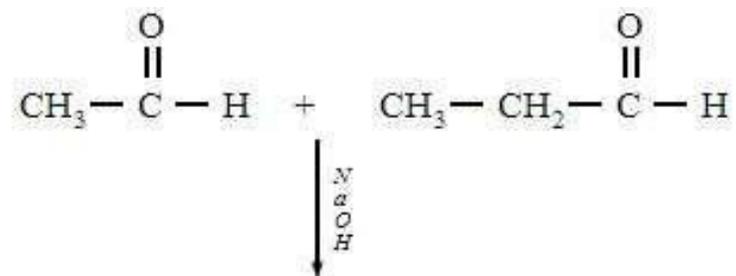
Aldehydes and ketones having α -hydrogen atom when treated with dilute alkali, form β -hydroxy aldehydes and β -hydroxy ketones respectively (known as aldols), which on heating give unsaturated compounds.



Cross aldol condensation

When aldol condensation is carried out with two different aldehydes or ketones having α -hydrogen, the reaction is called cross-aldol condensation. Cross-aldol condensation can take place between :

- Two different aldehyde groups
- Two different ketone groups
- One aldehyde and one ketone groups



5. Other reactions

Cannizzaro Reaction

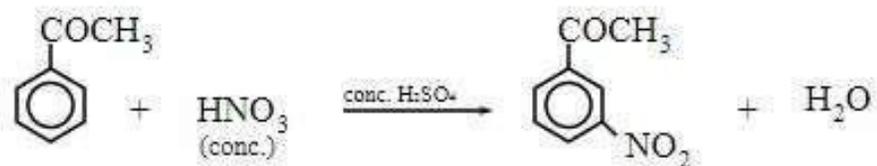
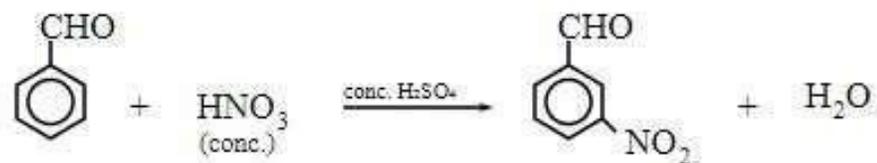
Aldehydes that do not have any α -hydrogen undergo disproportionation i.e., self oxidation-reduction, on treatment with concentrated alkali solution.



Electrophilic Substitution Reaction

Aromatic aldehydes and ketones undergo electrophilic substitution reactions such as nitration, sulphonation and halogenation. Since the aldehydic group (-CHO) and ketonic group (-COR or -COAr) are electron-withdrawing, they are deactivating and m-directing.

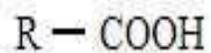
Nitration



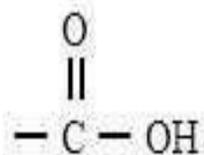
Carboxylic acid

Organic compounds containing -COOH as the functional group are called **carboxylic acids**. The -COOH group is called **carboxyl group**.

Carboxylic acid



Carboxyl group



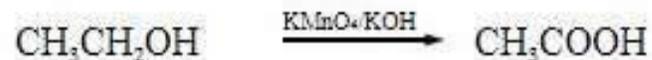
Preparation of Carboxylic Acids

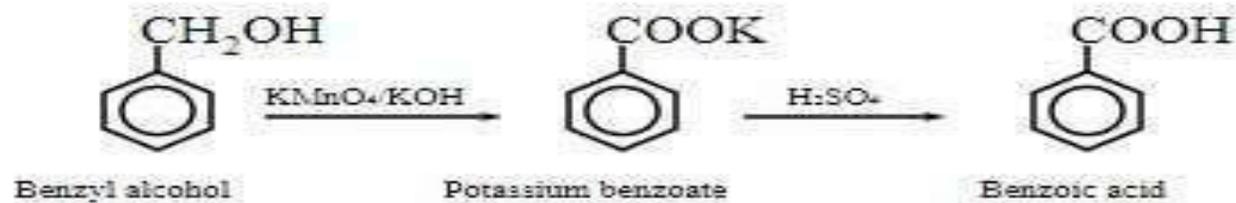
1. From primary alcohols and aldehydes

Primary alcohols and aldehydes are oxidised to corresponding carboxylic acids with oxidising agents such as :

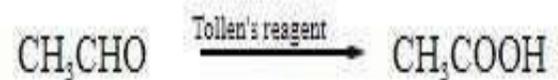
- KMnO_4 (neutral or acidic or alkaline)
- $\text{CrO}_3\text{-H}_2\text{SO}_4$ (Jones reagent)
- $\text{K}_2\text{Cr}_2\text{O}_7$ (acidic)

Acidified $\text{K}_2\text{Cr}_2\text{O}_7$ and Jones reagents often give some amount of esters; therefore, neutral or alkaline KMnO_4 is preferred for this purpose.



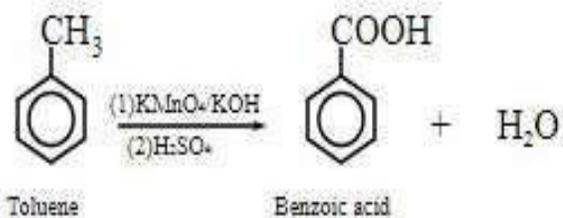


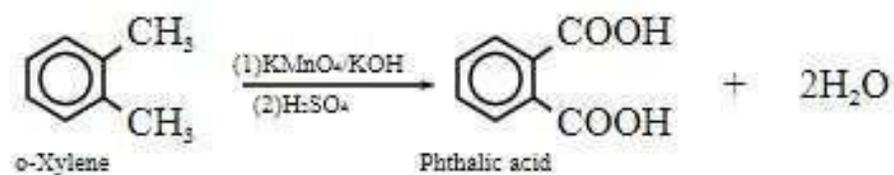
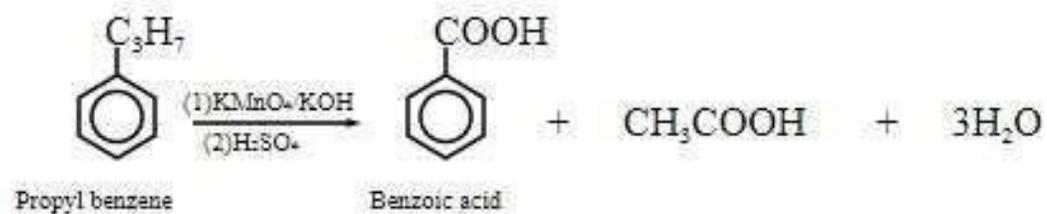
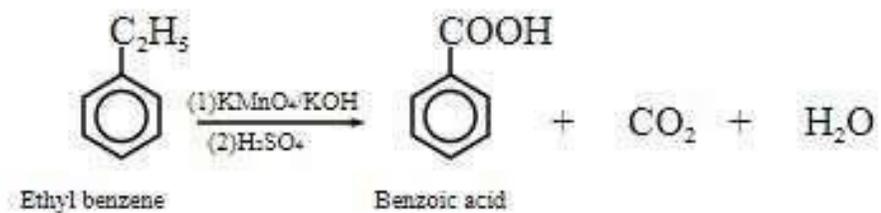
From aldehydes : Besides the above reagents, aldehydes are easily oxidised to carboxylic acids with mild oxidising agents such as Tollen's reagents.



2. From alkylbenzenes

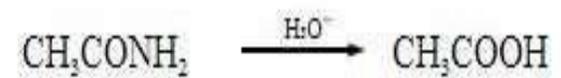
Aromatic carboxylic acids are prepared by oxidation of alkylbenzenes with alkaline permanganate. The side chain of alkylbenzene is oxidised to -COOH irrespective of the length of the chain; the side products, however, are different depending upon the alkyl group. Take a close look at the following reactions :



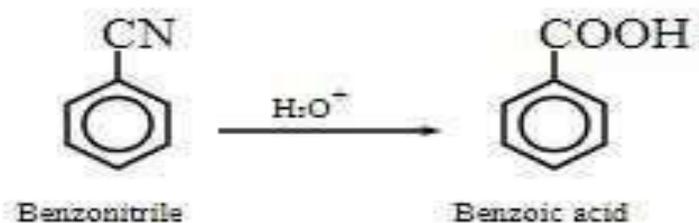
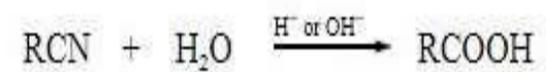


3. From nitriles and amides

Amides on hydrolysis yield carboxylic acids.

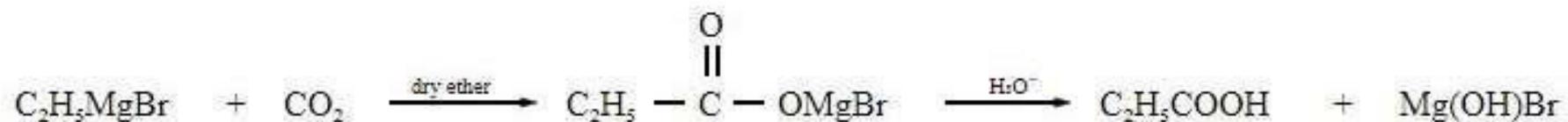
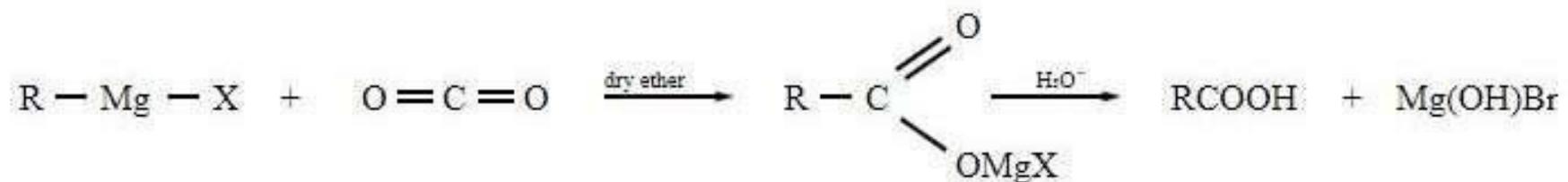


Hydrolysis of nitriles with H^+ or OH^- as catalysts yields carboxylic acids.



4. From Grignard reagents

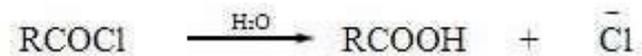
The reaction of grignard reagents with crushed dry ice (solid carbon dioxide) followed by acidification with mineral acids gives carboxylic acids.



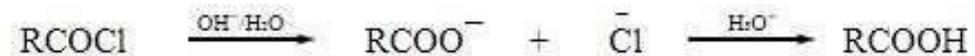
5. From acyl halides and anhydrides

Hydrolysis of acid chlorides yields carboxylic acids. It can be done in the following ways :

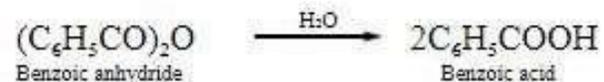
- Hydrolysis of acid chlorides with water gives carboxylic acids :



- Hydrolysis of acid chlorides with base followed by acidification gives carboxylic acids :

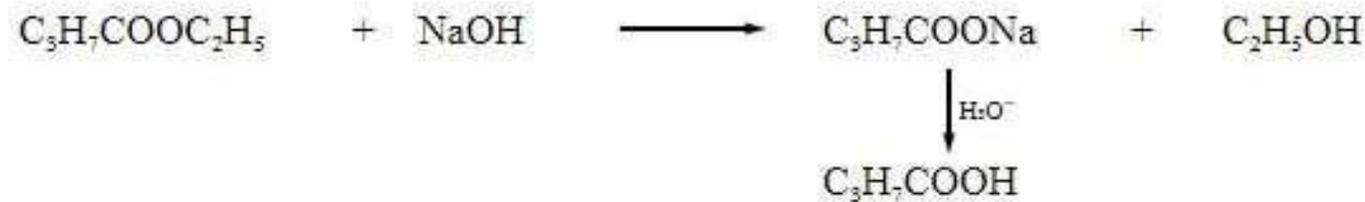
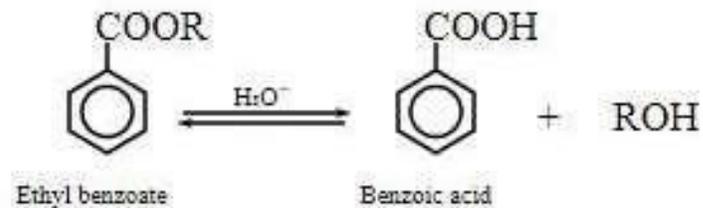


Similarly, hydrolysis of acid anhydrides yields carboxylic acids.



6. From esters

Hydrolysis of esters either with mineral acids or alkalies gives carboxylic acid. Acidic hydrolysis of esters directly gives carboxylic acids while the basic one gives carboxylates, which upon acidification yield carboxylic acids.



Physical Properties of Carboxylic Acids

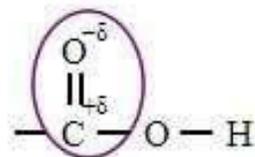
Boiling point of Carboxylic Acids

The boiling point of carboxylic acid is higher than those of aldehydes, ketones and alcohols of comparable molecular masses because carboxylic acids form very strong hydrogen bonds.

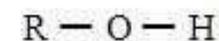
Why is the boiling point of carboxylic acid higher than that of alcohols even though both of them form H-bonds?

1. The O-H bond in carboxylic acid is attached to the electron withdrawing carbonyl group; therefore, the O-H bond in carboxylic acid is more polarised as compared to the O-H group of alcohols.

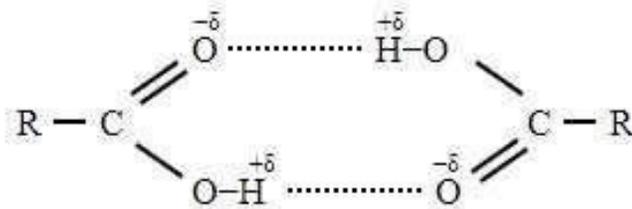
-O-H in carboxylic acid



-O-H in alcohol



2. Since the oxygen atom of the carbonyl group is polar, it can form H-bonds with the hydrogen atom of the O-H of the other molecule. These hydrogen bonds are so strong that they do not break completely even in the vapour phase. As a result, most carboxylic acids exist as **dimer** in the vapour phase or in the aprotic solvents.



Solubility of Carboxylic Acids

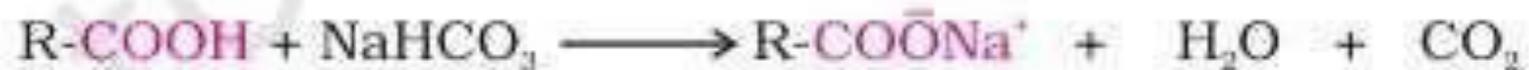
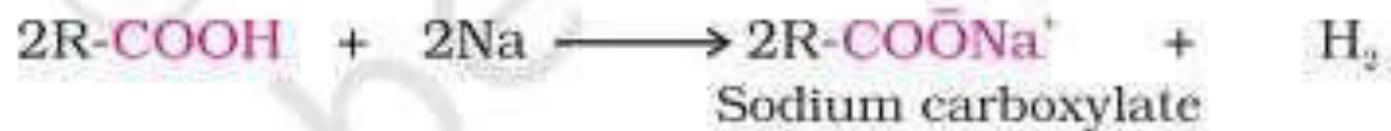
Solubility in water : Carboxylic acids containing up to four carbon atoms are miscible in water because they form H-bond with water. The solubility decreases with increase in the number of carbon atoms as the larger hydrocarbon part resists the formation of H-bonds. Benzoic acid is nearly insoluble in cold water because of the larger hydrocarbon part.

Solubility in organic solvents : Carboxylic acids are soluble in less polar organic solvents such as benzene, ether, alcohols etc.

Reactions of Carboxylic Acids Involving -OH

Reactions Involving Cleavage of O–H Bond

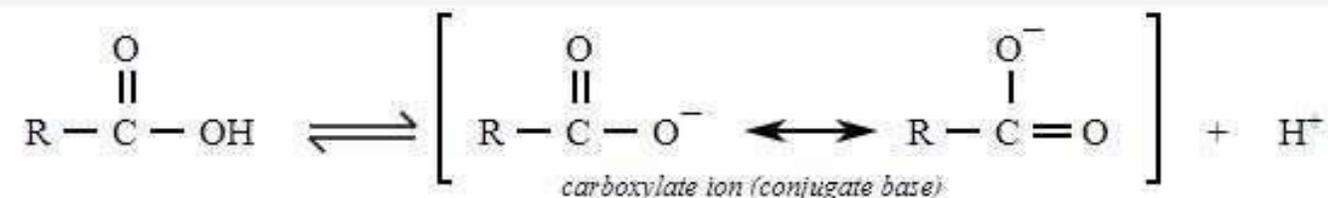
Acidity Reactions with metals and alkalies



Why are carboxylic acids stronger acids than alcohols?

Carboxylic acids are stronger acids than alcohols because the conjugate base (product left after the removal of hydrogen) of carboxylic acid is stabilised by resonance.

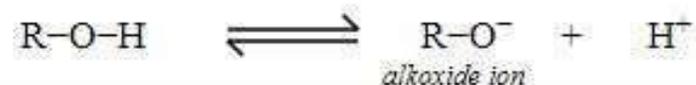
Carboxylate ion (conjugate base of carboxylic acids)



Since the carboxylate ion is stabilised by resonance, it is easier for carboxylic acids to release a proton to form carboxylate ion.

Alkoxide ion, on the other hand, does not exhibit resonance; therefore, it is less stable.

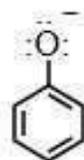
Alkoxide ion (conjugate base of alcohols)



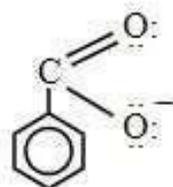
In other words, alcohols do not release protons easily to form less stable alkoxide ion; therefore, alcohols are less acidic.

Let us compare the first two structures of phenoxide ion with the resonance structures of carboxylate ions :

Phenoxide ion



Carboxylate ion



In phenoxide ion, the negative charge on oxygen atom is localized (i.e., sticks to the same oxygen atom) whereas in carboxylate ion, the negative charge is delocalized; therefore, carboxylate ion is more resonance stabilized. Thus, the release of a proton from carboxylic acids is much easier than phenols. In other words, **carboxylic acids are stronger acids than phenols.**

Effect of substitution on acidity of carboxylic acids :

- Electron attracting groups (-I groups) increase the acidity of carboxylic acids. Some electron attracting groups in order of their increasing -I-effect are given below :



- Electron releasing groups (+I groups) decrease acidity.

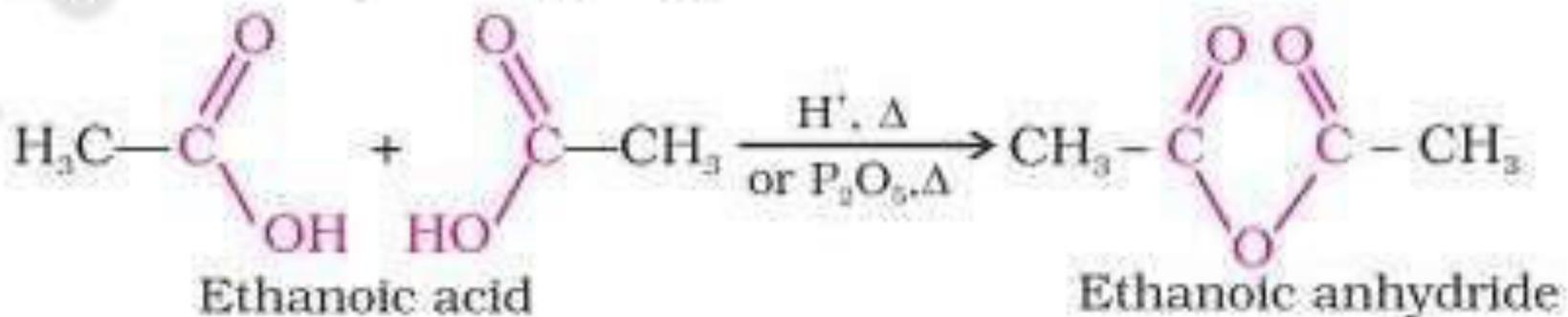
Increasing order of +I-effect



Reactions Involving Cleavage of C–OH Bond

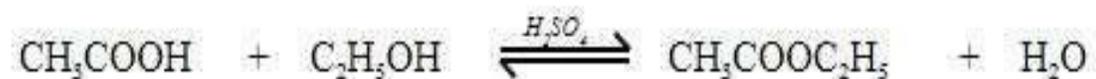
1. Formation of anhydride

Carboxylic acids on heating with mineral acids such as H_2SO_4 or with P_2O_5 give corresponding anhydride.



2. Esterification

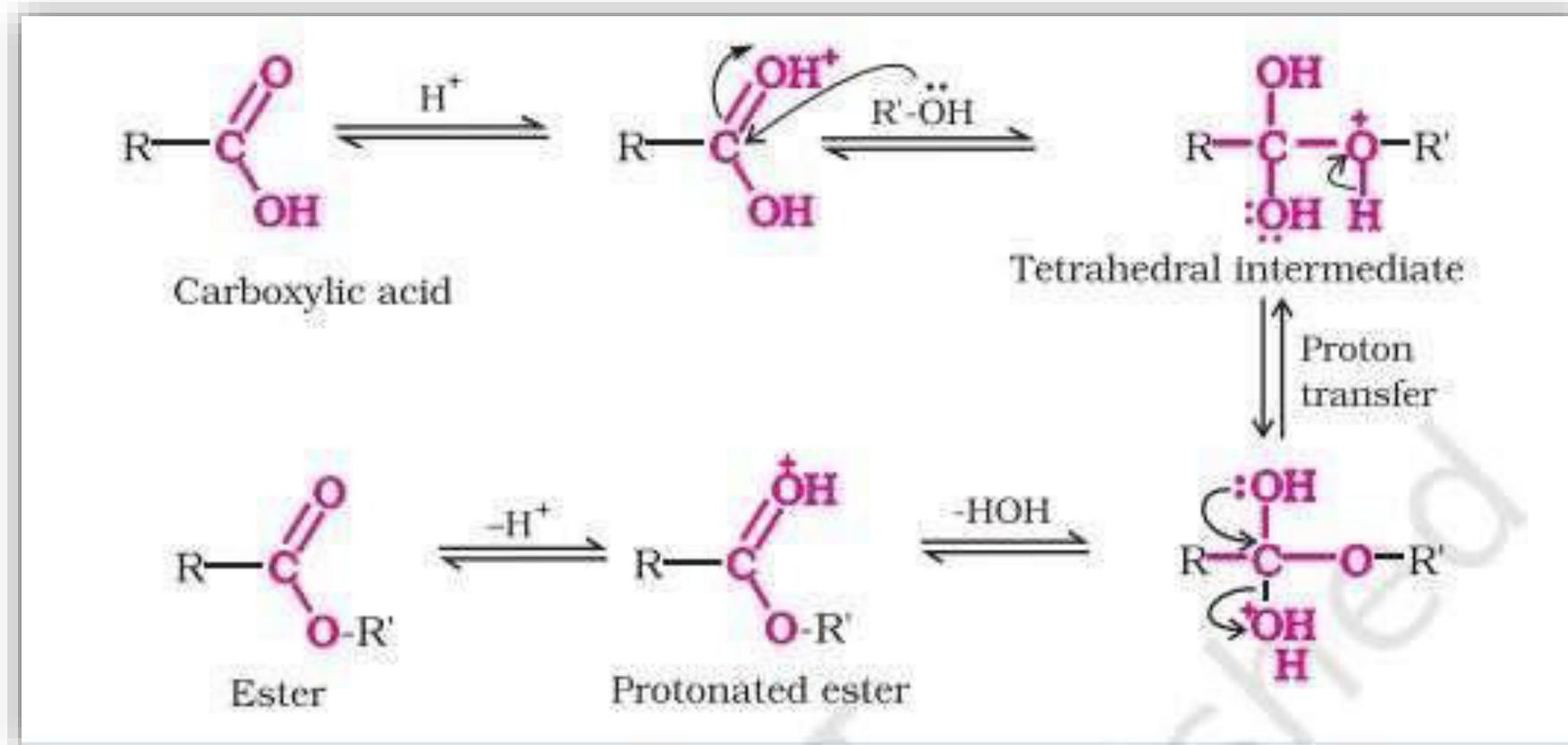
When acids are warmed with alcohols in the presence of conc. H_2SO_4 (or dry HCl), pleasant fruity smelling esters are formed.



Important points regarding esterification

- conc. H_2SO_4 acts as dehydrating agent.
- Since the reaction is an equilibrium reaction, ester is distilled off to shift the equilibrium in forward reaction.

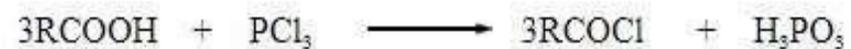
Mechanism of Esterification



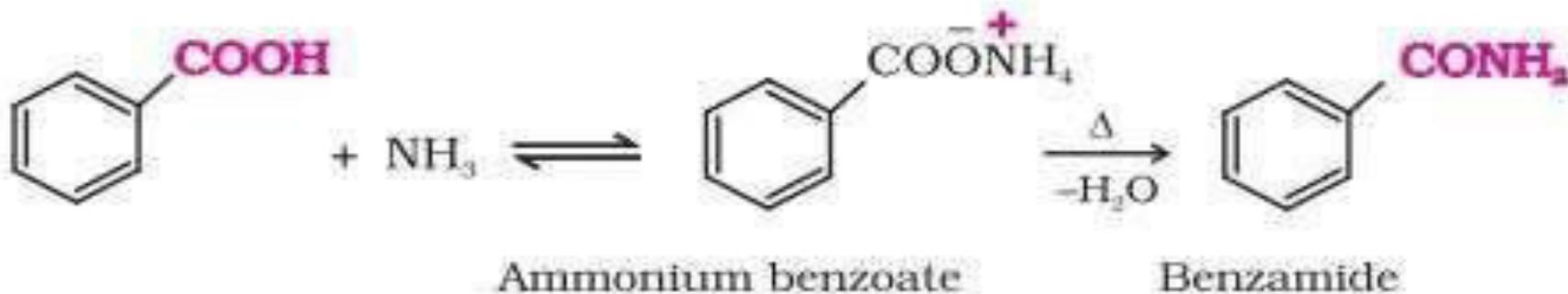
3. Reactions with PCl_5 , PCl_3 and SOCl_2

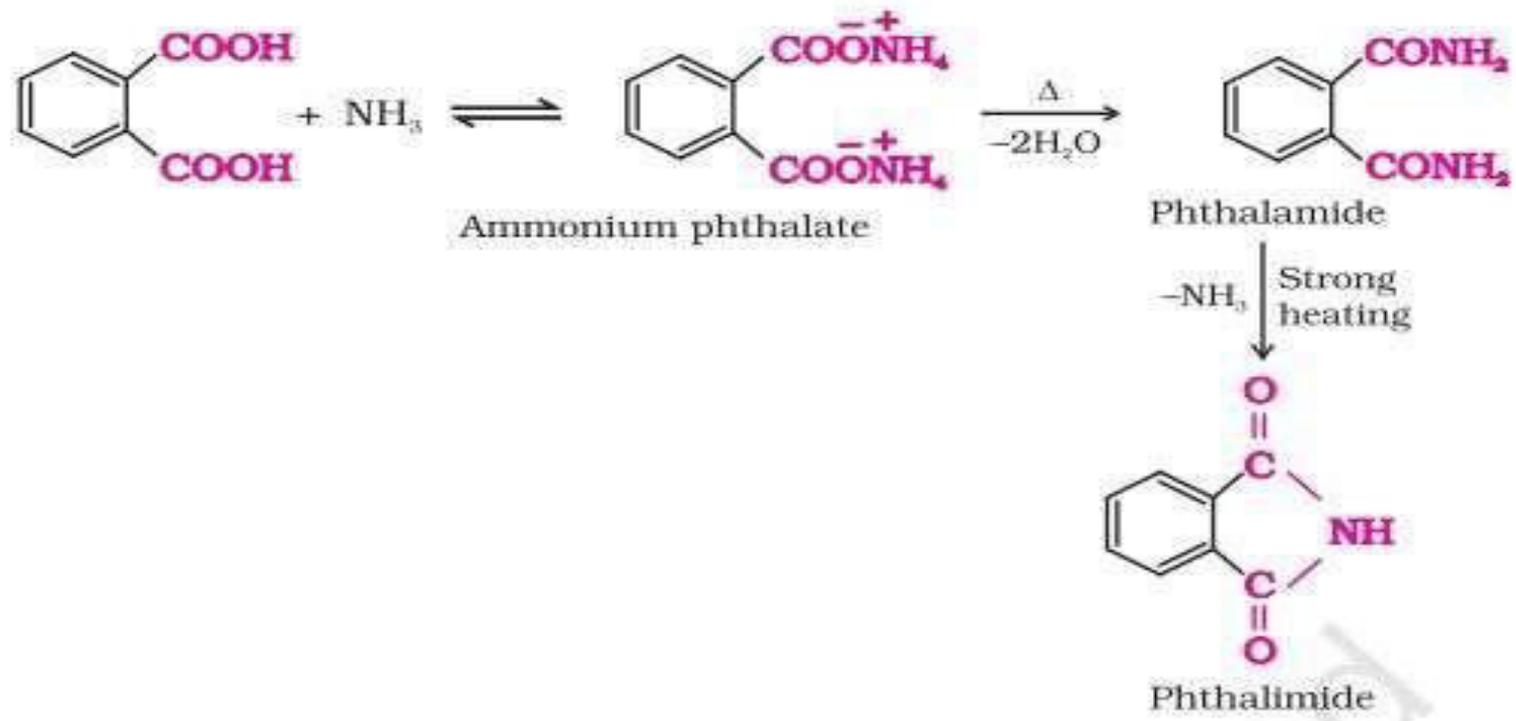
Formation of Acid Chlorides

Carboxylic acids react with PCl_5 , PCl_3 or SOCl_2 (thionyl chloride) to give acid chlorides



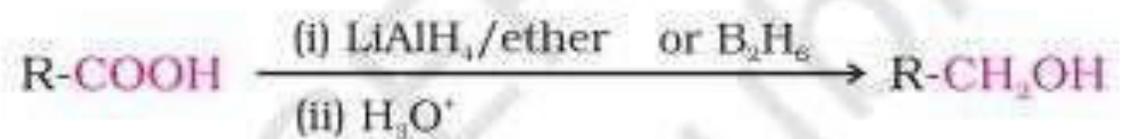
4. Reaction with ammonia





Reactions Involving –COOH Group

1. Reduction



2. Decarboxylation

Sodium salts of carboxylic acids undergo decarboxylation to form alkanes when distilled with soda lime (NaOH + CaO).

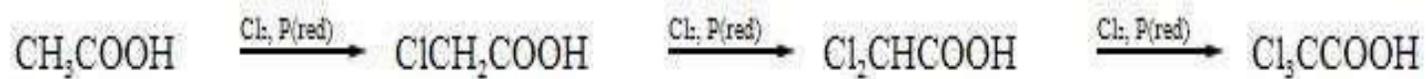


Substitution Reactions in the Hydrocarbon Part

1. Halogenation

Hell-Volhard Zelinsky (H.V.Z)

α -substituted carboxylic acids are formed when carboxylic acids react with Cl_2 or Br_2 in the presence of red phosphorus. This reaction is known as **Hell-Volhard Zelinsky reaction** or in short **H.V.Z reaction**.



Important points regarding Hell-Volhard Zelinsky reaction

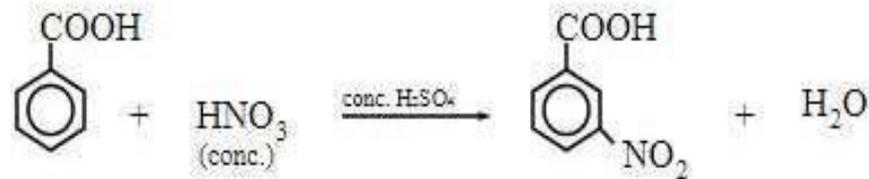
- Since formic acid (HCOOH) does not have any alkyl group, it does not undergo this reaction.

2. Ring substitution

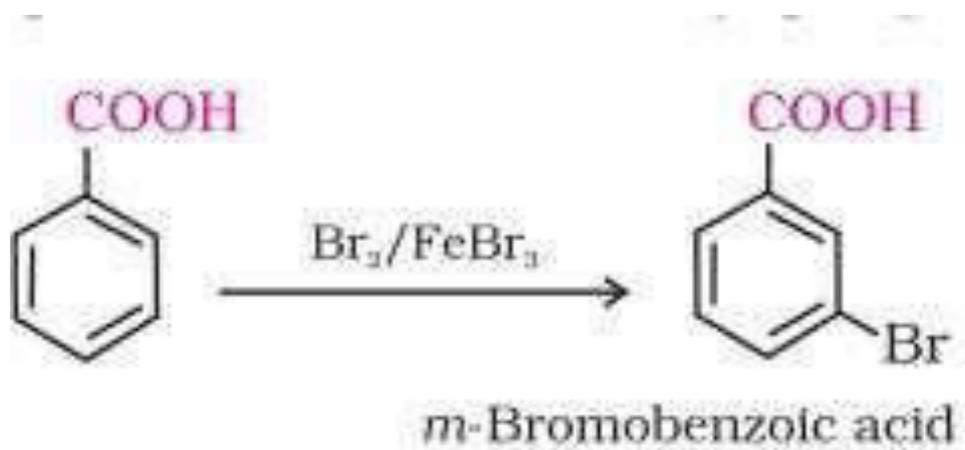
Electrophilic Substitution Reactions in Aromatic Acids

Aromatic carboxylic acids undergo electrophilic substitution reactions such as halogenation, nitration and sulphonation. Since the -COOH group is electron-withdrawing, the substitution occurs at meta position. The -COOH group is deactivating, therefore, the reactions take place under drastic conditions.

Nitration



Bromination



Friedel-Crafts reactions

Benzoic acid does not undergo Friedel-Crafts reactions because -COOH group is strong electron attracting group and deactivates benzene ring for alkylation and acylation.

An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogensulphite and give positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acid. Write the possible structure of the compound.



Department of Chemistry

**Govt Dr Shyama Prasad Mukharjee Science and Commerce
College [Old Benazeer College]**

Chemical Equilibrium

Presented By

Dr. Sudhanshu dhar Dwivedi

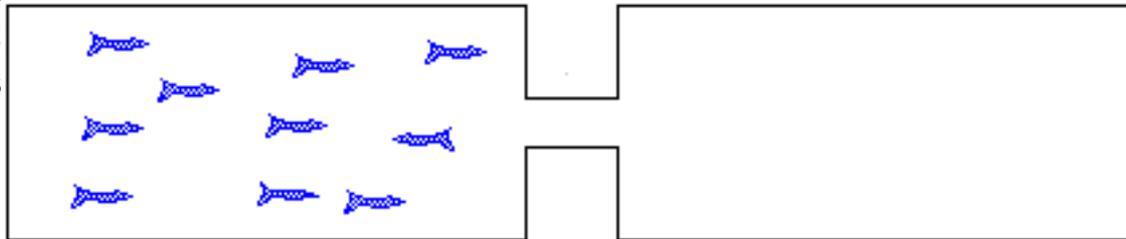
Chemical Equilibrium

Reversible

Not
subst
subst

10 fish

0 fish



ons two or more
back the original
o reform A and B.



A reaction which can go in the forward and backward direction simultaneously is called a reversible reaction.

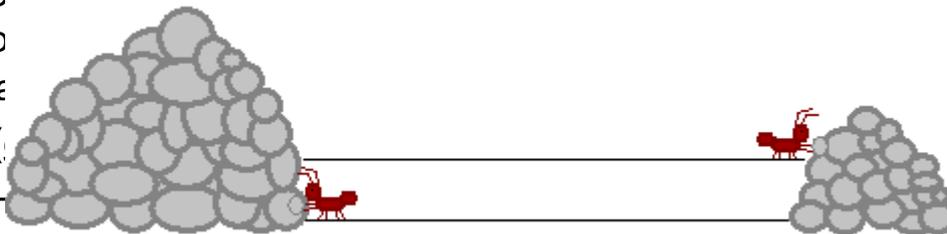
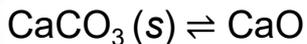
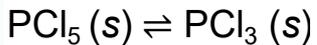
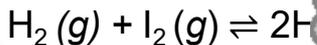
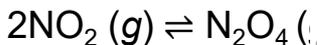


Such a reaction
products. The arro
the reverse reactio

Reactants

reactants and
ting left shows

A few common ex:



Products

Chemical Equilibrium

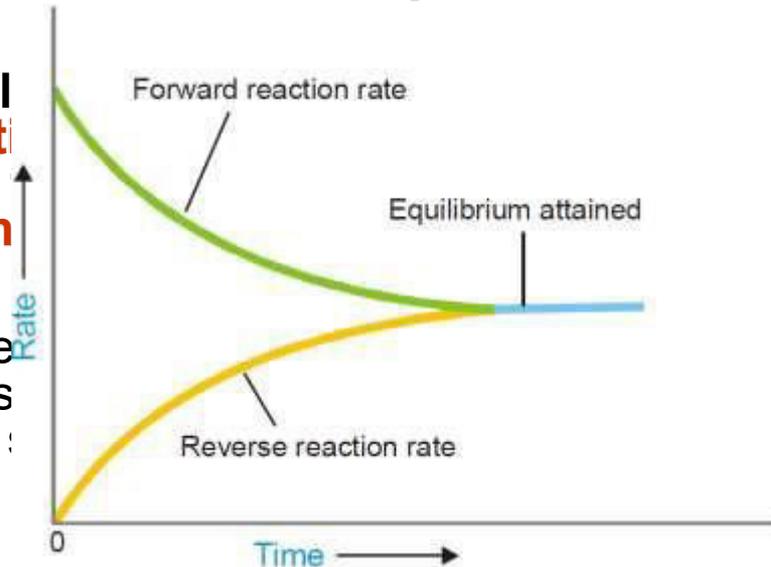
Let us consider the reaction,



If we start with A and B in a closed vessel, the forward reaction proceeds to form C and D. The concentrations of A and B decrease and those of C and D increase continuously. As a result the rate of forward reaction also decreases and the rate of the reverse reaction increases. Eventually, the rate of the two opposing reactions equals and the system attains a **state of equilibrium**.

Thus, **Chemical reversible reactions reach the same rate and do not change with**

Furthermore, the rates of both sides are equal. Thus, the concentrations of reactants and products are the same.



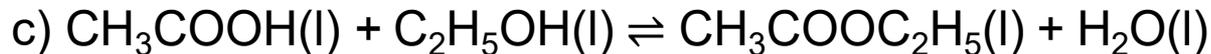
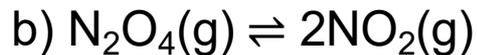
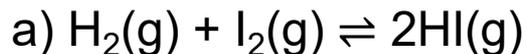
the state of a dynamic equilibrium is reached when the rates of the forward and reverse reactions are equal and the concentrations of reactants and products do not change.

Equilibrium can be attained from either side of the reaction, starting from the reactants (A and B) or from the products (C and D).

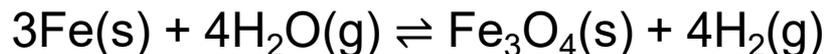
Types of Chemical Equilibrium

Depending on the phases of reaction species, chemical equilibrium can be divided into two types. They are-

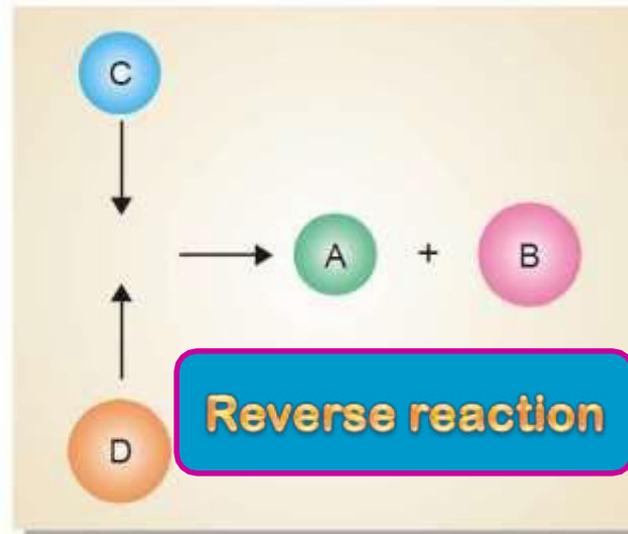
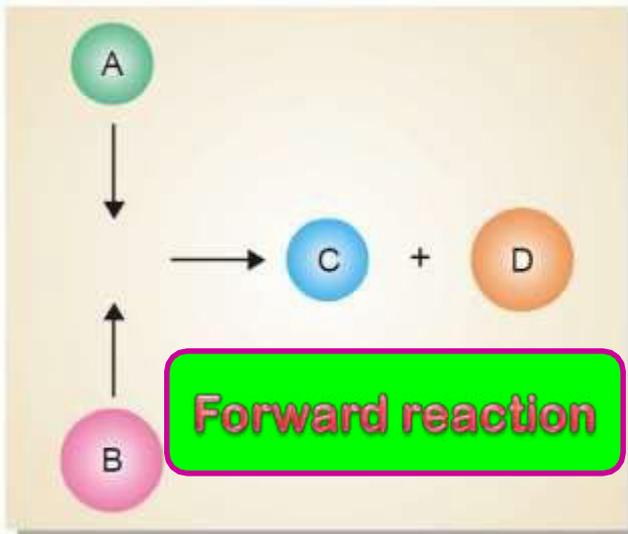
1) Homogenous Equilibrium: The equilibrium reaction in which all the reactants and products remain in the same phase is called a homogeneous equilibrium. For example



2) Heterogeneous Equilibrium : The equilibrium reaction in which all the reactants and products are not in the same phase is called a heterogeneous equilibrium. For example,



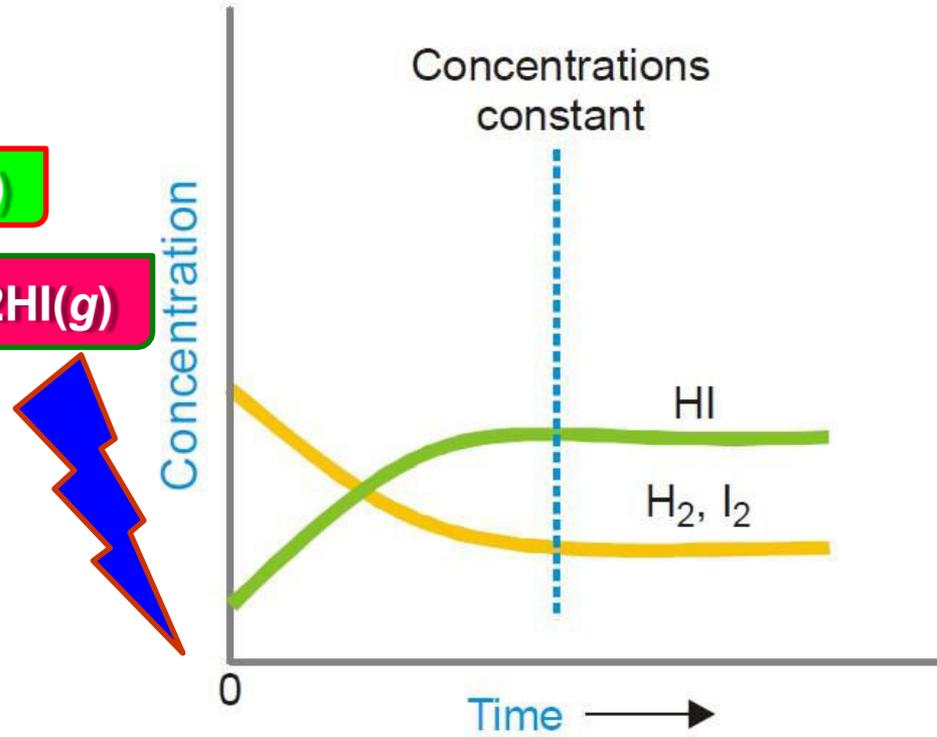
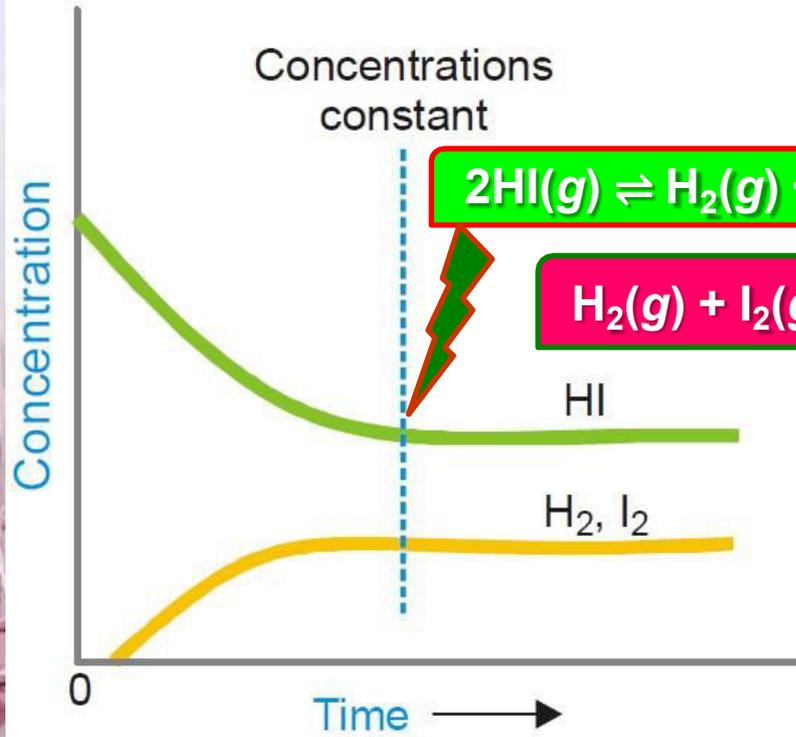
Chemical



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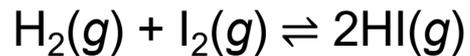
equilibrium,
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The dynamic nature of chemical equilibrium can be easily understood on the basis of the **kinetic molecular model**. The molecules of A and B in the equilibrium mixture collide with each other to form C and D. Likewise C and D collide to give back A and B. The collision of molecules in a closed system is a **ceaseless phenomenon**. Therefore collisions of A and B giving C and D (Forward reaction) and collisions of C and D giving back A and B (reverse reaction) continue to occur even at equilibrium, while concentrations remain unchanged.



(2) Equilibrium can be initiated from either side

The state of equilibrium of a reversible reaction can be approached whether we start with reactants or products. For example, the equilibrium is established if we start the reaction with H₂ and I₂ or 2HI.





(3) Equilibrium cannot be attained in an open vessel.

The equilibrium can be established only if the reaction vessel is closed and no part of the reactants or products is allowed to escape out. In an open vessel, the gaseous reactants and/or products may escape into the atmosphere leaving behind no possibility of attaining equilibrium.

However, the equilibrium can be attained when all the reactants and products are in the same phase. e.g. ethanol and ethanoic acid.

(4) A catalyst cannot change the equilibrium point.

When a catalyst is added to a system in equilibrium, it speeds up the rate of both the forward and the reverse reaction to an equal extent. Therefore, a catalyst cannot change the equilibrium point except that it is achieved earlier. This enhances the rate of the reaction.

(5) Value of equilibrium constant does not depend upon the initial concentration of reactants.

It has been found that equilibrium constant must be the same when the concentrations of reacting species are varied over a wide range.

LAW OF MASS ACTION

Two Norwegian chemists, Guldberg and Waage, studied experimentally a large number of equilibrium reactions. In 1864, they postulated a generalisation called the **law of mass action**.

It states that: **the rate of a chemical reaction is proportional to the active masses of the reactants.**

By the term '**active mass**' is meant the **molar concentration** *i.e.*, number of moles per litre. It is expressed by enclosing the formula of the substance in square brackets.

Mathematical Expression of Law of Mass Action

Let us consider a general reaction



And let [A], [B], [C] and [D] represent the molar concentrations of A, B, C and D at the equilibrium point.

Mathematical expression of law of mass action

According to the Law of Mass action,

$$\text{Rate of forward reaction} \propto [A][B] = k_1 [A][B]$$

$$\text{Rate of reverse reaction} \propto [C][D] = k_2 [C][D]$$

Where, k_1 and k_2 are rate constants for the forward and reverse reactions.

At equilibrium, rate of forward reaction = rate of reverse reaction.

$$\text{Therefore, } k_1 [A][B] = k_2 [C][D]$$

$$\text{or, } \frac{k_1}{k_2} = \frac{[C][D]}{[A][B]} \dots \dots \dots (1)$$

At any specific temperature k_1/k_2 is constant since both k_1 and k_2 are constants.

The ratio k_1/k_2 is called **Equilibrium constant** and is represented by the symbol **K_c** , or simply **k_c** . The subscript '**c**' indicates that the value is in terms of concentrations of reactants and products. The equation (1) may be written as

$$\text{Equilibrium constant, } k_c = \frac{[C][D] - \text{Product Concentrations}}{[A][B] - \text{Reactant Concentrations}}$$





Consider the reaction,



Here, the forward reaction is dependent on the collisions of each of two A molecules. Therefore, for writing the equilibrium expression, each molecule is regarded as a separate entity *i.e.*,



Then the equilibrium constant expression is-

$$K_c = \frac{[C][D]}{[A][A]} = \frac{[C][D]}{[A]^2} \text{ - Power Equal to Coefficient of A}$$

As a general rule, if there are two or more molecules of the same substance in the chemical equation, **its concentration is raised to the power equal to the numerical coefficient of the substance in the equation.**

Equilibrium Constant Expression for a Reaction in General Terms

The general reaction may be written as-



where a , b , c and d are numerical coefficients of the substances A, B, C and D respectively. The equilibrium constant expression is-

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Where, K_c is the **equilibrium constant**. The general definition of the equilibrium constant may thus be stated as: **the product of the equilibrium concentrations of the products divided by the product of the equilibrium concentrations of the reactants, with each concentration term raised to a power equal to the numerical coefficient of the substance in the balanced equation.**



PROBLEMS



 **PROBLEM-1:** Give the equilibrium constant expression for the reaction, $\text{N}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{NH}_3(\text{g})$

 **PROBLEM-2:** Write the equilibrium constant expression for the reaction, $\text{N}_2\text{O}_5(\text{g}) \rightleftharpoons \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$

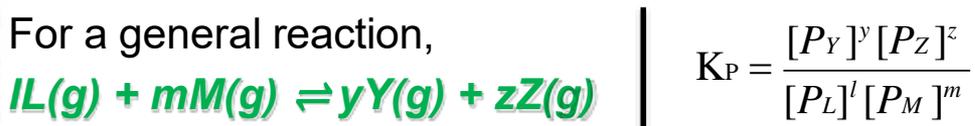
Equilibrium Constant Expression in Terms of Partial Pressures

When all the reactants and products are gases, we can also formulate the equilibrium constant expression in terms of partial pressure. The relationship between the partial pressure (p) of any one gas in the equilibrium mixture and the molar concentration follows from the general ideal gas equation

$$PV = nRT \text{ or, } P\left(\frac{n}{V}\right)RT$$

The quantity n/V is the number of moles of the gas per unit volume and is simply the molar concentration.

Thus, $P = (\text{Molar concentration}) \times RT$. *i.e.*, **the partial pressure of a gas in the equilibrium mixture is directly proportional to its molar concentration at a given temperature.** Therefore, we can write the equilibrium constant expression in terms of partial pressure instead of molar concentrations.



Here, K_p is the equilibrium constant, the subscript p referring to partial pressure. Partial pressures are expressed in atmospheres.



Relationship Between K_p and K_c

Let us consider a general reaction,



Where, j , k , l and m are numerical coefficients of the substance, A, B, C and D respectively. And let $[A]$, $[B]$, $[C]$ and $[D]$ represent the molar concentrations of A, B, C and D at the equilibrium point.

The equilibrium constant expression is,
$$K_C = \frac{[C]^l [D]^m}{[A]^j [B]^k} \dots\dots\dots(1)$$

Where, all reactants and products are gases. We can write the equilibrium constant expression in terms of partial pressures as-
$$K_P = \frac{[P_C]^l [P_D]^m}{[P_A]^j [P_B]^k} \dots\dots\dots(2)$$

Assuming that all these gases constituting the equilibrium mixture obey the ideal gas equation, the partial pressure (p) of a gas is-

$$P = \left(\frac{n}{V} \right) RT$$

Where, n/V is the molar concentration. Thus, the partial pressures of individual gases A, B, C and D are: $P_A = [A] RT$; $P_B = [B] RT$; $P_C = [C] RT$; $P_D = [D] RT$





Substituting these values in equation (2), we have-

$$K_P = \frac{[C]^l [RT]^l [D]^m [RT]^m}{[A]^j [RT]^j [B]^k [RT]^k}$$

$$\text{or, } K_P = \frac{[C]^l [D]^m}{[A]^j [B]^k} \times \frac{[RT]^l [RT]^m}{[RT]^j [RT]^k}$$

$$\text{or, } K_P = \frac{[C]^l [D]^m}{[A]^j [B]^k} \times \frac{[RT]^{l+m}}{[RT]^{j+k}}$$

$$\text{or, } K_P = K_C \times [RT]^{(l+m)-(j+k)}$$

$$\text{or, } K_P = K_C \times [RT]^{\Delta n}$$

$$\therefore K_P = K_C \times [RT]^{\Delta n} \dots\dots(3)$$

Where, $\Delta n = (l + m) - (j + k)$, is the difference in the sums of the coefficients for the gaseous products and reactants. From the expression (3) it is clear that when $\Delta n = 0$, $K_p = K_c$.



Mathematical problem:

💣* At 500°C , the reaction between N_2 and H_2 to form ammonia has

$K_c = 6.0 \times 10^{-2}$. *What is the numerical value of K_p for the reaction?*

💣* The value of K_p at 25°C for the reaction $2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{NOCl}(\text{g})$ is $1.9 \times 10^3 \text{ atm}^{-1}$.

Calculate the value of K_c at the same temperature.

Units of equilibrium constant

In the equilibrium expression for a particular reaction, the concentrations are given in units of moles/litre or mol/L, and the partial pressure are given in atmospheres (atm). The units of K_c and K_p , depend on the specific reaction.

(1) When the total number of moles of reactants and products are equal.

In the equilibrium expression of these reactions, the concentration or pressure terms in the numerator and denominator exactly cancel out. Thus, K_c or K_p for such a reaction is without units.

Taking example of the reaction,



$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(\text{mol/L})^2}{(\text{mol/L})(\text{mol/L})} \text{ (No units)}$$

$$K_p = \frac{[P_{\text{HI}}]^2}{[P_{\text{H}_2}][P_{\text{I}_2}]} = \frac{(\text{atm})^2}{(\text{atm})(\text{atm})} \text{ (No units)}$$



(2) When the total number of moles of the reactants and products are unequal.

In such reactions K_c will have units $(\text{mol/litre})^n$ and K_p will have units $(\text{atm})^n$, where n is equal to the total number of moles of products minus the total number of moles of reactants.

Thus, for the reaction: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

So, the units for K_C are mol/L and K_P units are atm.

$$K_C = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(\text{mol/L})^2}{(\text{mol/L})} = (\text{mol/L})$$

$$K_P = \frac{[P_{\text{NO}_2}]^2}{[P_{\text{N}_2\text{O}_4}]} = \frac{(\text{atm})^2}{(\text{atm})} = (\text{atm})$$

For the reaction : $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

Units for K_C are and K_P may be found as follows

Thus,
units of K_C are $\text{mol}^{-2} \text{L}^2$ and
units of K_p are atm^{-2} .

$$K_C = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(\text{mol/L})^2}{(\text{mol/L})(\text{mol/L})^3} = \text{mol}^{-2}/\text{L}^2$$

$$K_P = \frac{[P_{\text{NH}_3}]^2}{[P_{\text{H}_2}][P_{\text{N}_2}]^3} = \frac{(\text{atm})^2}{(\text{atm})(\text{atm})^3} = (\text{atm})^{-2}$$

HOMOGENEOUS EQUILIBRIA

Liquid Systems (Liquid equilibria)

The chemical equilibrium in which all the reactants and products are in the liquid phase, are referred to as the liquid equilibria.

Like the gas-phase equilibria, the liquid equilibria are also called homogeneous equilibria.

For example, alcohols and acids react to form esters and water.



Let us start with **a** mole of acetic acid and **b** moles of alcohol.

If **x** moles of acetic acid react with **x** moles of ethyl alcohol, **x** moles of ester and **x** moles of water are produced when the equilibrium is established.



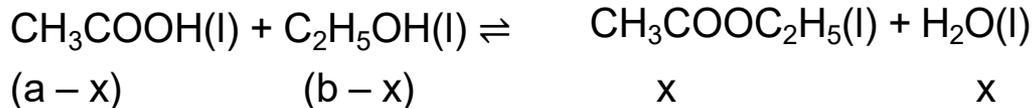
Now the moles present at equilibrium are:

$$\text{CH}_3\text{COOH} = (a - x) \text{ moles}$$

$$\text{C}_2\text{H}_5\text{OH} = (b - x) \text{ moles}$$

$$\text{CH}_3\text{COOC}_2\text{H}_5 = x \text{ moles}$$

$$\text{H}_2\text{O} = x \text{ moles}$$



$$[\text{CH}_3\text{COOH}] = \frac{a - x}{V}$$

$$[\text{C}_2\text{H}_5\text{OH}] = \frac{b - x}{V}$$

$$[\text{CH}_3\text{COOC}_2\text{H}_5] = \frac{x}{V}$$

$$[\text{H}_2\text{O}] = \frac{x}{V}$$

If V liter be the total volume of the equilibrium mixture, the concentrations of the various species are:

The equilibrium constant expression may be written as

$$K = \frac{\frac{x}{V} \times \frac{x}{V}}{\frac{a-x}{V} \times \frac{b-x}{V}} \quad \text{or, } K = \frac{x^2}{(a-x)(b-x)}$$

It may be noted that the volume terms V in the numerator and denominator cancel out. **In liquid systems when there is a change in the number of moles as a result of the reaction, it is necessary to consider the volume V while calculating the equilibrium constant K .**

Heterogeneous Equilibria

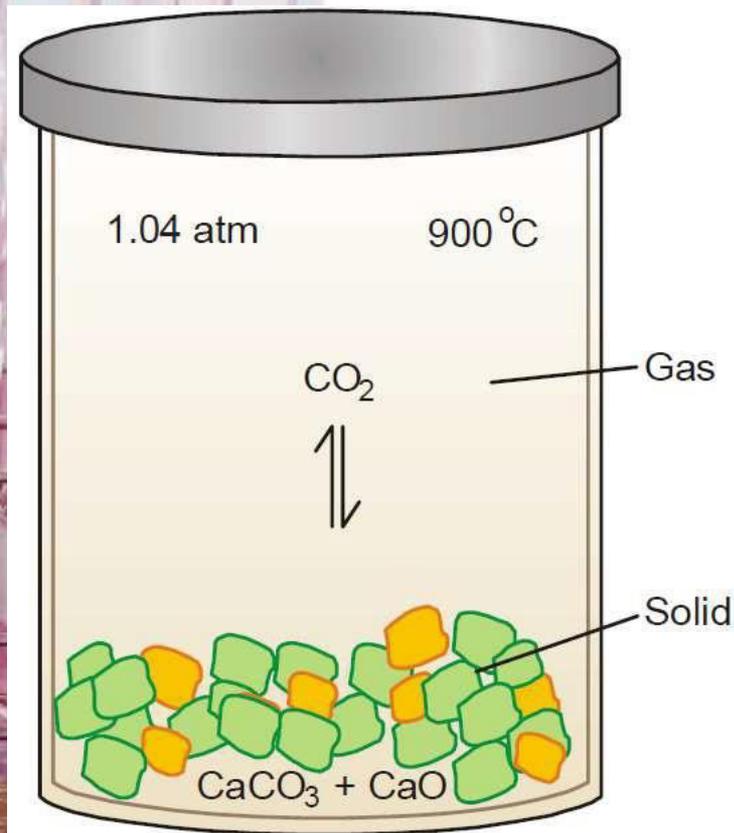
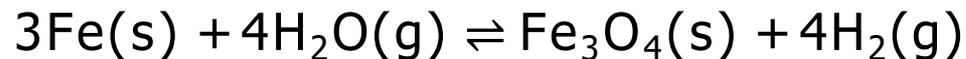
Chemical equilibria in which the reactants and products are not all in the same phase is called **heterogeneous equilibria**.

Example: The decomposition of calcium carbonate upon heating to form calcium oxide and carbon dioxide.

If the reaction is carried in a closed vessel, the following equilibrium is established.



Other examples:



Le Chatelier's Principle

In 1884, the French Chemist Henry Le Chatelier proposed a general principle which applies to all systems in equilibrium. The principle states that-

“When a system is at equilibrium a change in any one of the factors upon which the equilibrium depends will cause the equilibrium to shift in a direction such that the effect of the change is diminished.”

There are **three ways in** which the change can be caused on a chemical equilibrium:

(1) Changing the concentration of a reactant or product.

(2) Changing the pressure (or volume) of the system.

(3) Changing the temperature.



Thus, when applied to a chemical reaction in equilibrium, Le Chatelier's principle can be stated as: **if a change in concentration, pressure or temperature is caused to a chemical reaction in equilibrium, the equilibrium will shift to the right or the left so as to minimize the change.**

What is Equilibrium?



This is not Equilibrium?



Effect of a Change in Concentration

We can restate Le Chatelier's principle for the special case of concentration changes: **when concentration of any of the reactants or products is changed, the equilibrium shifts in a direction so as to reduce the change in concentration that was made.**

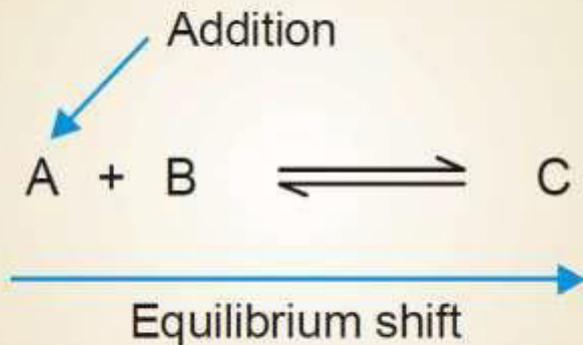
A change in the concentration of a reactant or product can be effected by the addition or removal of that species.

Let us consider a general reaction,



When a reactant, say, **A** is added at equilibrium, its concentration is increased.

The forward reaction alone occurs momentarily. According to Le Chatelier's principle, a new equilibrium will be established so as to reduce the concentration of **A**. Thus, the addition of A causes the equilibrium to shift to right. This increases the concentration (yield) of the product **C**.



Equilibrium I

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$$[\text{N}_2] = 0.399 \text{ M}$$

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$$[\text{H}_2] = 1.197 \text{ M}$$

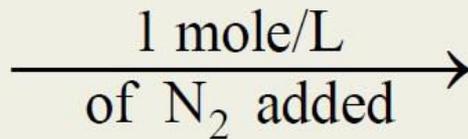
$$[\text{NH}_3] = 0.202 \text{ M}$$

Equilibrium II

$$\text{N}_2 = 1.348 \text{ M}$$

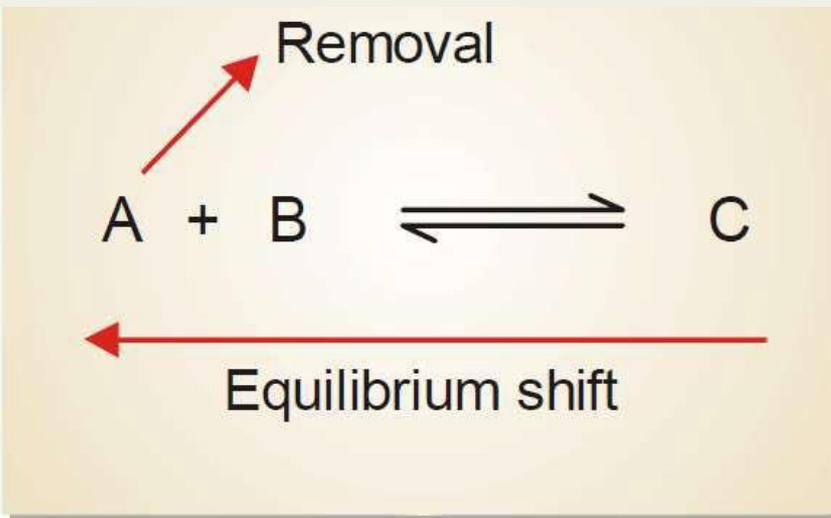
$$[\text{H}_2] = 1.044 \text{ M}$$

$$[\text{NH}_3] = 0.304 \text{ M}$$



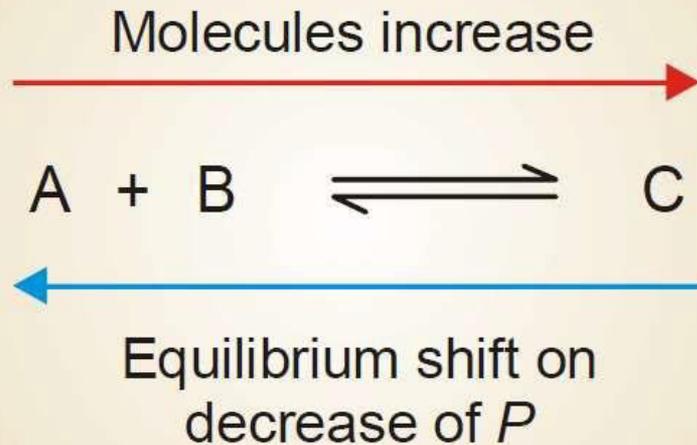
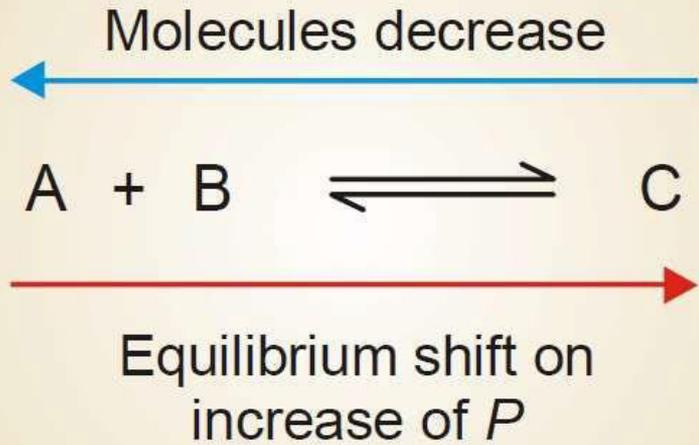
When N_2 (or H_2) is added to an equilibrium system, the equilibrium will shift to the right (Le Chatelier's principle). The concentration of NH_3 will increase. The results in a particular case are given below.

Obviously, the addition of a reactant shifts the equilibrium to the right, increasing the concentration of the products. In this case, the concentration of NH_3 increases from 0.202 M to 0.304 M.



When N_2 is removed from an equilibrium system, the equilibrium will shift to the left (Le Chatelier's principle). The concentration of NH_3 will decrease. The results in a particular case are given below.

Obviously, the removal of a reactant shifts the equilibrium to the left, decreasing the concentration of the products. In this case, the concentration of NH_3 decreases from 0.304 M to 0.202 M.



Let us consider a reaction,



The combination of A and B produces a decrease of number of molecules while the decomposition of C into A and B results in the increase of molecules. Therefore, by the increase of pressure on the equilibrium it will shift to right and give more C. A decrease in pressure will cause the opposite effect. The equilibrium will shift to the left when C will decompose to form more of A and B.



The reactions in which the number of product molecules is equal to the number of reactant molecules, are unaffected by pressure changes.

For example, $\text{H}_2 (\text{g}) + \text{I}_2 (\text{g}) \rightleftharpoons 2\text{HI} (\text{g})$

In such a case, the system is unable to undo the increase or decrease of pressure.

In light of the above discussion, we can state a general rule to predict the effect of pressure changes on chemical equilibria.

The increase of pressure on a chemical equilibrium shifts it in that direction in which the number of molecules decreases and vice-versa.



EFFECT OF A CHANGE IN TEMPERATURE

Chemical reactions consist of two opposing reactions.

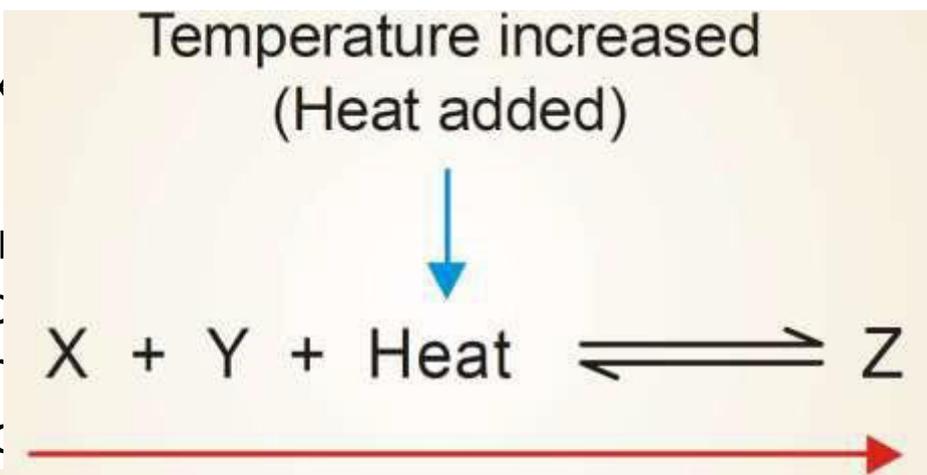
If the forward reaction proceeds by the evolution of heat (exothermic), the reverse reaction occurs by the absorption of heat (endothermic).

Both these reactions take place at the same time and equilibrium exists between the two. If temperature of a reaction is raised, heat is added to the system. The equilibrium shifts in a direction in which heat is absorbed in an attempt to lower the temperature. Thus, the effect of temperature on an equilibrium reaction can easily be predicted by the following version of the Le Chatelier's principle.

When temperature of a reaction is increased, the equilibrium shifts in a direction in which heat is absorbed.

Let us consider an ex

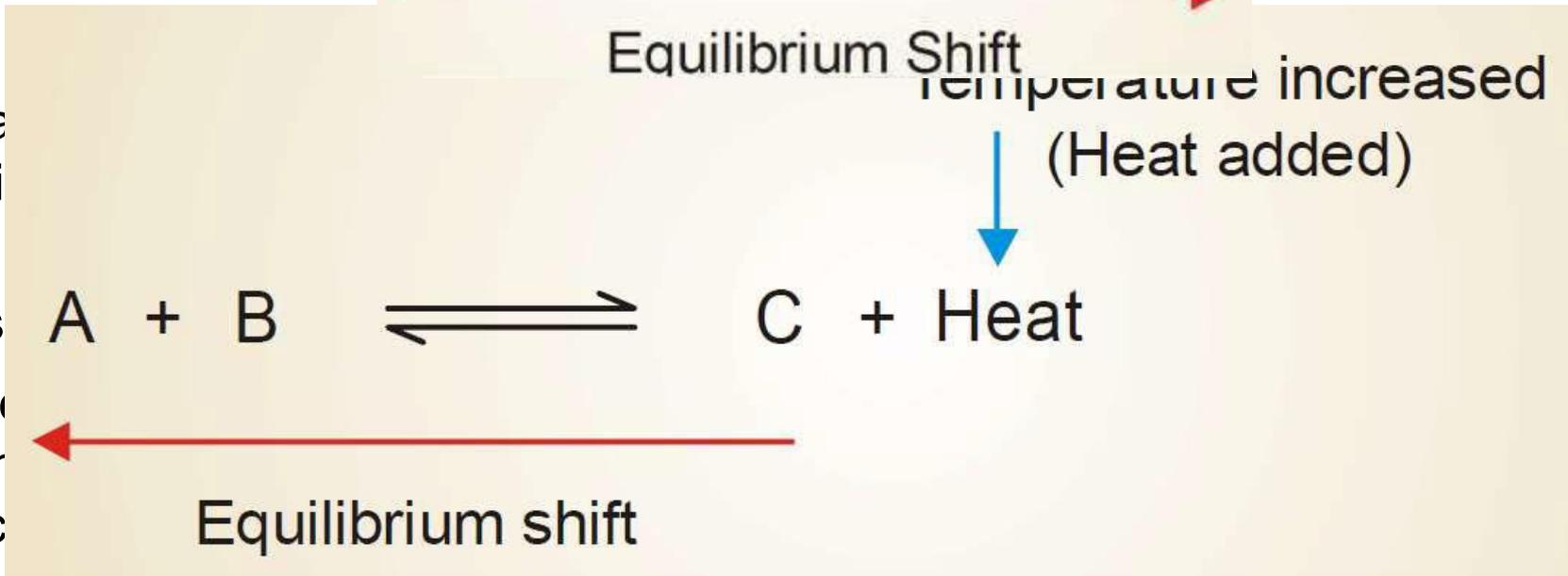
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Formation of Ammonia from N₂ and H₂

The synthesis of ammonia from nitrogen and hydrogen is an exothermic reaction.



When the temperature of the system is raised, the equilibrium will shift from right-to-left which absorbs heat (*Le Chatelier's principle*). This results in the lower yield of ammonia.

On the other hand, by lowering the temperature of the system, the equilibrium will shift to the right which evolves heat in an attempt to raise the temperature. This would increase the yield of ammonia.

But with decreasing temperature, the rate of reaction is slowed down considerably and the equilibrium is reached slowly.

Thus, in the commercial production of ammonia, it is not feasible to use temperature much lower than 500°C. At lower temperature, even in the presence of a catalyst, the reaction proceeds too slowly to be practical.



Conditions for Maximum Yield in Industrial Processes

With the help of Le Chatelier's principle we can work out the optimum conditions for securing the maximum yield of products in industrial processes.

Synthesis of Ammonia (*Haber Process*)

The manufacture of ammonia by Haber process is represented by the equation-



A look at the equation provides the following information:

(a) The reaction is exothermic

(b) The reaction proceeds with a decrease in the number of moles.

(1)Low temperature. By applying Le Chatelier's principle, low temperature will shift the equilibrium to the right. This gives greater yield of ammonia. In actual practice a temperature of about **450°C** is used when the percentage of ammonia in the equilibrium mixture is 15.

(2)High pressure. High pressure on the reaction at equilibrium favors the shift of the equilibrium to the right. This is so because the forward reaction proceeds with a decrease in the number of moles. A pressure of about **200 atmospheres** is applied in practice.

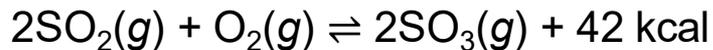
(3)Catalyst. As already stated, low temperature is necessary for higher yield of ammonia. But at relatively low temperatures, the rate of reaction is slow and the equilibrium is attained in a long time. To increase the rate of reaction and thus quicken the attainment of equilibrium, a catalyst is used. Finely divided **iron containing molybdenum** is employed in actual practice.

Molybdenum acts as a promoter that increases the life and efficiency of the catalyst.

Pure N_2 and H_2 gases are used in the process. Any impurities in the gases would poison the catalyst and decrease its efficiency.

Manufacture of Sulphuric Acid (*Contact Process*)

The chief reaction used in the process is-



Following information is revealed by the above equation:

- (a) The reaction is exothermic.
- (b) The reaction proceeds with a decrease in number of moles.

On the basis of Le Chatelier's principle, the conditions for the maximum yield can be worked out as below:

(1)Low temperature. Since the forward reaction is exothermic, the equilibrium will shift on the right at low temperature. An optimum temperature between **400-450°C** is required for the maximum yield of sulphur trioxide.

(2)High pressure. Since the number of moles is decreased in the forward reaction, increase of pressure will shift the equilibrium to the right. Thus, for maximum yield of SO_3 , **2 to 3 atmosphere** pressure is used.

(3)Catalyst. At the low temperature used in the reaction, the rate of reaction is slow and the equilibrium is attained slowly. A catalyst is, therefore, used to speed up the establishment of the equilibrium. **Vanadium pentoxide, V_2O_5** , is commonly used and it has replaced the earlier catalyst *platinum asbestos* which was easily poisoned by the impurities present in the reacting gases. All samples, SO_2 and O_2 used for the manufacture of sulphuric acid must be pure and dry.

Manufacture of Nitric Acid (*Birkeland-Eyde Process*)

Nitric acid is prepared on a large scale by making use of the reaction



The equation tells us that:

- (a) The reaction proceeds with no change in the number of moles.
- (b) The reaction is endothermic and proceeds by absorption of heat.

The favorable conditions for the maximum yield of NO are:

(1) High temperature. Since the forward reaction is endothermic, increase of temperature will favor it (Le Chatelier's principle). Thus, a high temperature of the order of 3000°C is employed to get high yield of nitric acid.

(2) No effect of pressure. Since the forward reaction involves no change in the number of moles, a change in pressure has no effect on the equilibrium.

(3) High concentration. The formation of nitric oxide is favored by using high concentrations of the reactants *i.e.* N_2 and O_2 .



thank
you!

Department of Chemistry

**Govt Dr Shyama Prasad Mukharjee Science and Commerce
College [Old Benazeer College]**

Topic:-Complex compounds

Presented By

Dr.Sudhanshu dhar Dwivedi

- Co-ordination Compounds: Complex compounds in which transition metals atoms are bound to a number of anions or neutral molecules.
- Co-ordination compounds follow the postulates put forth by Werner in 1898.

Difference between a double salt and a complex compound

Both double salts as well as complexes are formed by the combination of two or more stable compounds in stoichiometric ratio.

However, they differ in the fact that double salts such as Carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, Mohr's salt, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, potash alum, $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, etc.

dissociate into simple ions completely when dissolved in water.

However, complex ions such as $[\text{Fe}(\text{CN})_6]^{4-}$ of $\text{K}_4\text{Fe}(\text{CN})_6$, do not dissociate into Fe^{2+} and CN^- ions.

Some Important Definitions 1...

- *(a) Coordination entity*-A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules.
- *(b) Central atom/ion*-In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement around it, is called the central atom or ion.
- These central atoms/ions are also referred to as Lewis acids.

Some Important Definitions 2...

- *(c) Coordination number*-The coordination number (CN) of a metal ion in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded.
- It is important to note here that coordination number of the central atom/ion is determined only by the number of sigma bonds formed by the ligand with the central atom/ion.
- Pi bonds, if formed between the ligand and the central atom/ion, are not counted for this purpose.

Some Important Definitions 3...

- *(d) Coordination sphere*-The central atom/ion and the ligands attached to it are enclosed in square bracket and is collectively termed as the coordination sphere.
- *(e) Coordination polyhedron*-The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion defines a coordination polyhedron about the central atom.
- The most common coordination polyhedra are octahedral, square planar and tetrahedral.

Some Important Definitions 4...

- *(f) Oxidation number of central atom*-The oxidation number of the central atom in a complex is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom.
- *(g) Homoleptic and heteroleptic complexes*-
- Complexes in which a metal is bound to only one kind of donor groups, e.g., $[\text{Co}(\text{NH}_3)_6]^{3+}$, are known as *homoleptic*.
- *Complexes in which a metal is bound to more than one kind of donor groups, e.g., $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$, are known as heteroleptic.*

Ligands..

- The ions or molecules bound to the central atom/ion in the coordination entity are called ligands.
- These may be simple ions such as Cl^- , small molecules such as H_2O or NH_3 , larger molecules such as $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ or $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$ or even macromolecules, such as proteins.

Types of Ligands...

- When a ligand is bound to a metal ion through a single donor atom, as with Cl^- , H_2O or NH_3 , the ligand is said to be **Unidentate**.
- When a ligand can bind through two donor atoms as in $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ (ethane-1,2-diamine) or $\text{C}_2\text{O}_4^{2-}$ (oxalate), the ligand is said to be **Didentate**.
- When several donor atoms are present in a single ligand as in $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$, the ligand is said to be **Polydentate**.

Types of Ligands...

- When a di- or polydentate ligand uses its two or more donor atoms to bind a single metal ion, it is said to be a **chelate ligand**.
- The number of such ligating groups is called the **denticity** of the ligand.
- Ligand which can ligate through two different atoms is called **ambidentate ligand**.

Isomerism in Complex Compound

- Two types of isomerism :-
- Stereoisomerism and Structural Isomerism

Stereoisomer's

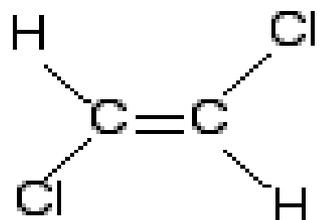
- (i) Geometrical
- (ii) Optical

Structural

- (i) Linkage
- (ii) Coordination
- (iii) Ionisation
- (iv) Solvate

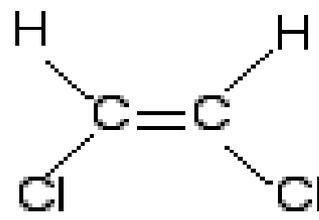
Geometrical Isomerism

- This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands
- Important examples of this behaviour are found with coordination numbers 4 and 6.
- In a square planar complex of formula $[MX_2L_2]$ (X and L are unidentate), the two ligands X may be arranged adjacent to each other in a *cis* isomer, or opposite to each other in a *trans isomer*



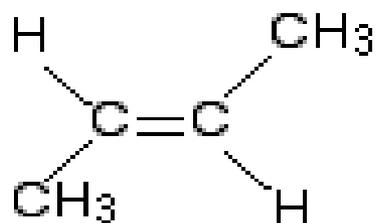
trans-1,2-dichloroethene

(*E*)-1,2-dichloroethene



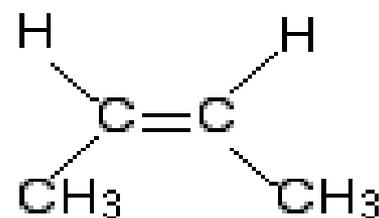
cis-1,2-dichloroethene

(*Z*)-1,2-dichloroethene



trans-but-2-ene

(*E*)-but-2-ene

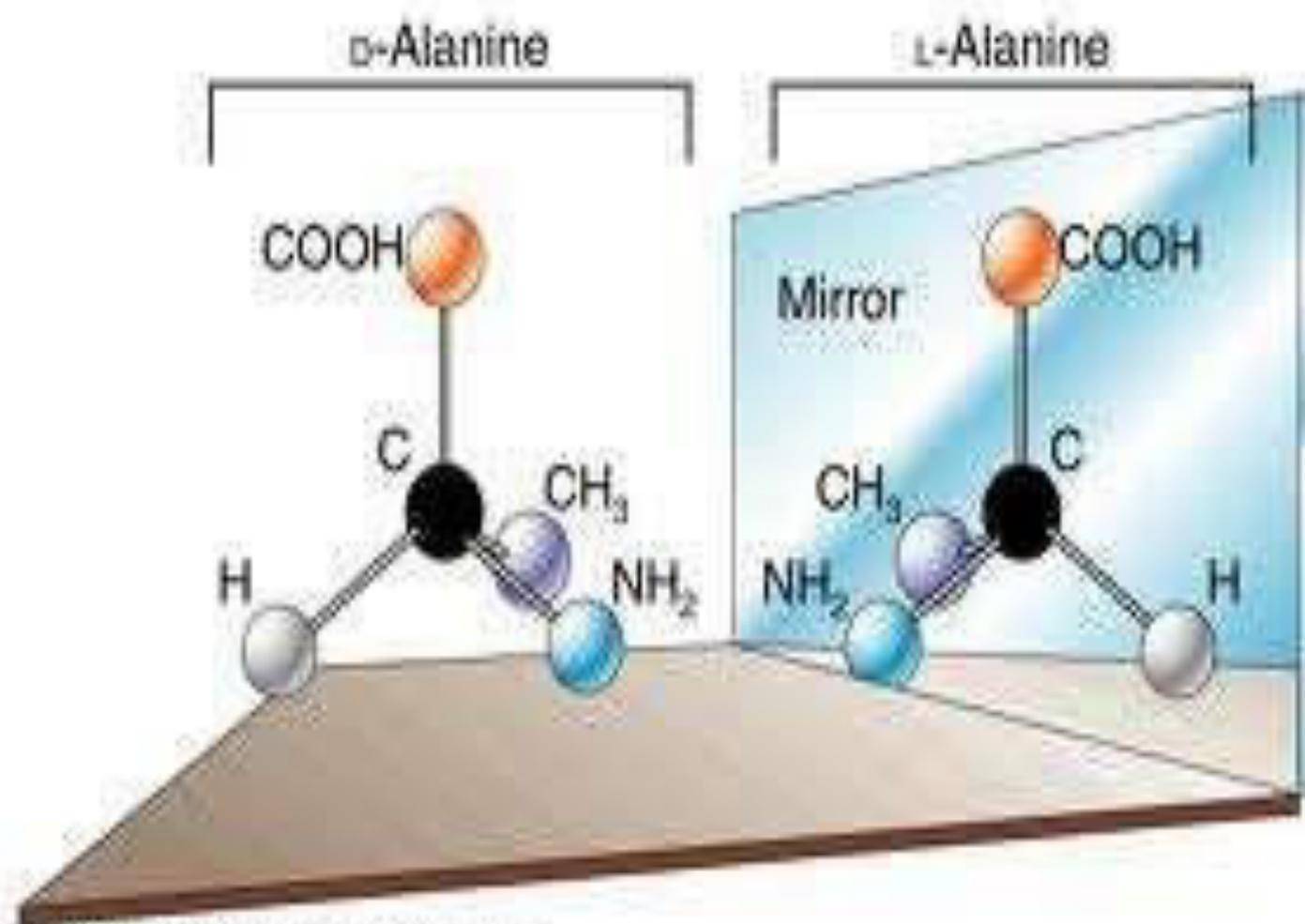


cis-but-2-ene

(*Z*)-but-2-ene

Optical Isomerism

- Optical isomers are mirror images that cannot be superimposed on one another. These are called as *enantiomers*.
- The two forms are called *dextro (d) and laevo (l) depending* upon the direction they rotate the plane of polarised light in a polarimeter (*d rotates to the right, l to the left*).
- Optical isomerism is common in octahedral complexes involving didentate ligands



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Linkage Isomerism

- Linkage isomerism arises in a coordination compound containing ambidentate ligand.
- A simple example is provided by complexes containing the thiocyanate ligand, NCS^- , which may bind through the nitrogen to give M-NCS or through sulphur to give M-SCN .
- Jørgensen discovered such behaviour in the complex $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$, which is obtained as the red form, in which the nitrite ligand is bound through oxygen ($-\text{ONO}$), and as the yellow form, in which the nitrite ligand is bound through nitrogen ($-\text{NO}_2$).

Coordination Isomerism

- This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex.
- An example is provided by $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$, in which the NH_3 ligands are bound to Co^{3+} and the CN^- ligands to Cr^{3+} .
- In its coordination isomer $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$, the NH_3 ligands are bound to Cr^{3+} and the CN^- ligands to Co^{3+} .

Ionisation Isomerism

- This form of isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion.
- An example is provided by the ionisation isomers $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ and $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$.

Solvate Isomerism

- This form of isomerism is known as 'hydrate isomerism' in case where water is involved as a solvent.
- Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice.
- An example is provided by the aqua complex $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (violet) and its solvate isomer $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (grey-green).

Importance and Applications

- The coordination compounds are of great importance.
- These compounds are widely present in the mineral, plant and animal worlds and are known to play many important functions in the area of analytical chemistry, metallurgy, biological systems, industry and medicine.
- Coordination compounds find use in many qualitative and quantitative chemical analysis.
- The familiar colour reactions given by metal ions with a number of ligands (especially chelating ligands), as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis.
- Examples of such reagents include EDTA, DMG (dimethylglyoxime), α -nitroso- β -naphthol, cupron, etc.

Importance & Applications

- Hardness of water is estimated by simple titration with Na_2EDTA .
- The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA. The selective estimation of these ions can be done due to difference in the stability constants of calcium and magnesium complexes.
- Some important extraction processes of metals, like those of silver and gold, make use of complex formation.
- Gold, for example, combines with cyanide in the presence of oxygen and water to form the coordination entity $[\text{Au}(\text{CN})_2]^-$ in aqueous solution. Gold can be separated in metallic form from this solution by the addition of zinc

Importance & Applications

- Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds.
- For example, impure nickel is converted to $[\text{Ni}(\text{CO})_4]$, which is decomposed to yield pure nickel.
- Coordination compounds are of great importance in biological systems.
- The pigment responsible for photosynthesis, chlorophyll, is a coordination compound of magnesium.
- Haemoglobin, the red pigment of blood which acts as oxygen carrier is a coordination compound of iron.
- Vitamin B12, cyanocobalamin, the anti-pernicious anaemia factor, is a coordination compound of cobalt.
- Among the other compounds of biological importance with coordinated metal ions are the enzymes like, carboxypeptidase A and carbonic anhydrase (catalysts of biological systems).

Importance & Application

- Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium complex, $[(\text{Ph}_3\text{P})_3\text{RhCl}]$, a Wilkinson catalyst, is used for the hydrogenation of alkenes.
- Articles can be electroplated with silver and gold much more smoothly and evenly from solutions of the complexes, $[\text{Ag}(\text{CN})_2]^-$ and $[\text{Au}(\text{CN})_2]^-$ than from a solution of simple metal ions.
- In black and white photography, the developed film is fixed by washing with hypo solution which dissolves the non decomposed AgBr to form a complex ion, $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$.

Medical Application

- There is growing interest in the use of chelate therapy in medicinal chemistry.
- An example is the treatment of problems caused by the presence of metals in toxic proportions in plant/animal systems.
- Thus, excess of copper and iron are removed by the chelating ligands
- D–penicillamine and desferrioxime B via the formation of coordination compounds.
- EDTA is used in the treatment of lead poisoning.
- Some coordination compounds of platinum effectively inhibit the growth of tumours.
- Examples are: *cis–platin and related compounds*.

THANKING YOU!

Grignard Reagent Preparation & Reactions

Dr. Sudhanshu Dhar Dwivedi
Professor of Chemistry

Grignard Reagent

- Grignard reagents are *extremely useful* organometallic compounds in the field of organic chemistry. They exhibit strong nucleophilic qualities and also have the ability to form new carbon-carbon bonds. Therefore, they display qualities that are also exhibited by organolithium reagents and the two reagents are considered similar.
- When the alkyl group attached to a Grignard reagent is replaced by an amido group, the resulting compound is called a Hauser base. These compounds are even more nucleophilic than their Grignard counterparts.

What are Grignard Reagents?

- A Grignard reagent is an organomagnesium compound which can be described by the ***chemical formula 'R-Mg-X'*** where R refers to an alkyl or aryl group and X refers to a halogen.
- They are generally produced by reacting an aryl halide or an alkyl halide with magnesium.
- These reagents were discovered by the **French chemist Victor Grignard**, who won the Nobel Prize in Chemistry in the year 1912 for his work on these compounds.

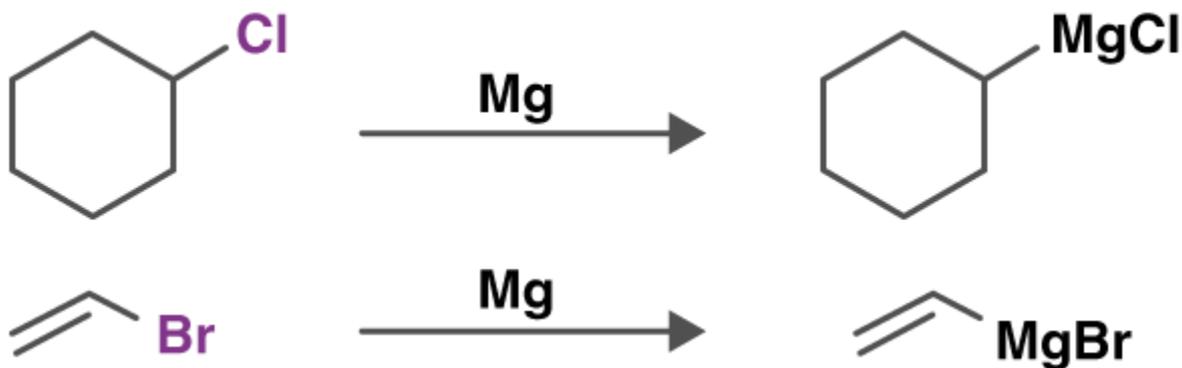
Grignard Reagents

- Reactions that form carbon-carbon bonds are among the most beneficial to synthetic organic chemist. In 1912, Victor Grignard was awarded the Nobel Prize in Chemistry for his discovery of a new sequence of reactions resulting in the creation of a carbon-carbon bond. Grignard synthesis involves the preparation of an organomagnesium reagent through the reaction of an alkyl bromide with magnesium metal.

Preparation of Grignard Reagents

- These reagents are prepared via the treatment of magnesium with organic halides such as alkyl or [aryl halides](#).
- This is done with the help of solvents comprising ethers (which are described by the formula R-O-R') because the ligands provided by these solvents help in the stabilization of the ***organomagnesium compound***.
- Water and air are very harmful to this synthesis and can quickly destroy the Grignard reagent which is being formed via protonolysis or via oxidation of the reagent. Therefore, the process must be carried out in air-free conditions.

An illustration detailing the preparation of these reagents is provided below.

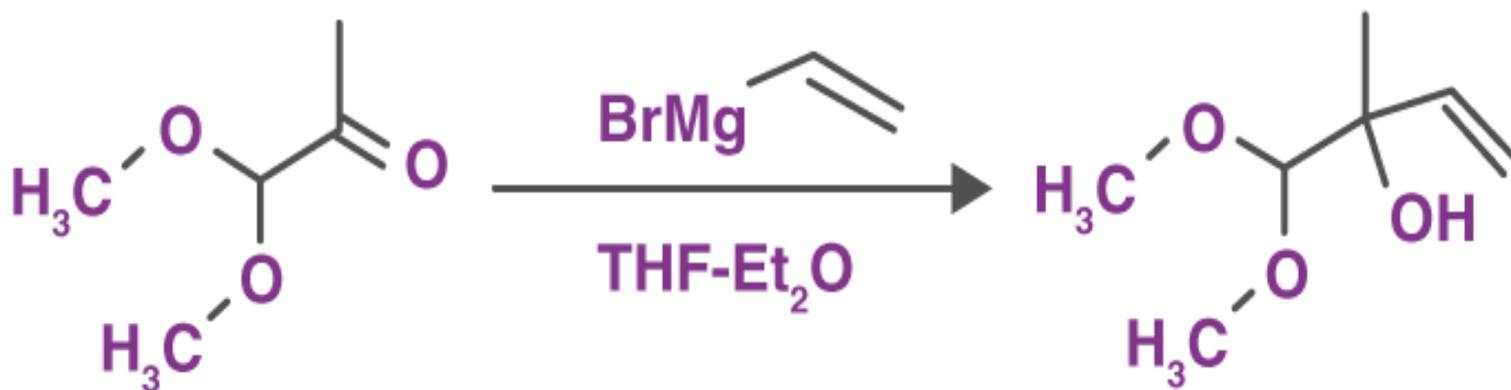


Reactions of Grignard Reagents

- During a reaction involving Grignard reagents, it is necessary to ensure that no water is present which would otherwise cause the reagent to decompose rapidly. Therefore, the majority of Grignard reactions occur in solvents such as anhydrous diethyl ether or tetrahydrofuran because the oxygen in these solvents stabilizes the magnesium reagent.
- Grignard reagents are very important reagents in organic chemistry since they can be reacted with a wide range of compounds to form different products. Some of the reactions of these reagents are listed below.

Reactions with Carbonyl Group

- These reagents form various products when reacted with different carbonyl compounds. The most common reaction of Grignard reagents is the alkylation of ketones and aldehydes with the help of R-Mg-X.



Reactions with Non-Carbon Electrophiles

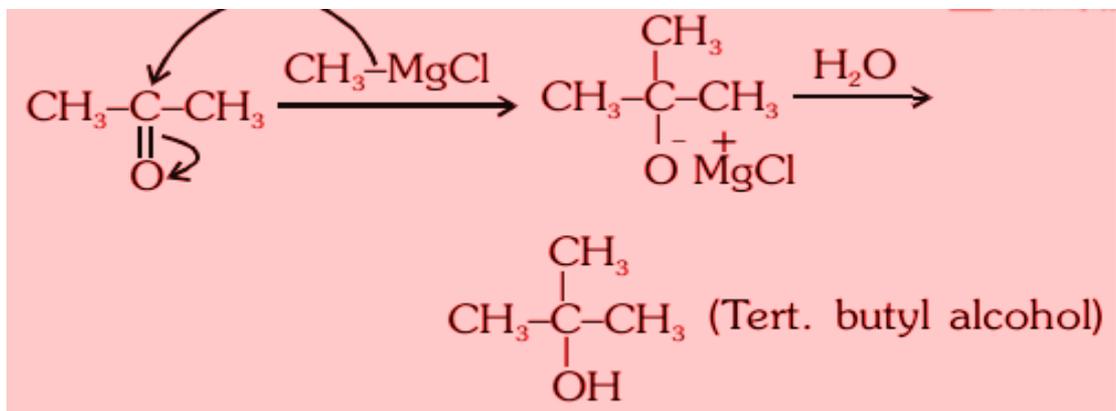
- For the *formation of new carbon-heteroatom bonds, Grignard reagents and some organolithium compounds are very useful.* These reagents can also undergo a transmetallation reaction with cadmium chloride, yielding dialkyl cadmium. This reaction can be written as follows.
- $2R-Mg-X + CdCl_2 \rightarrow R_2Cd + 2Mg(X)Cl$
- Alkyl chains can be attached to many metals and metalloids with the help of these reagents.

Reactions with Organic Halides

- Typically, these reagents are quite unreactive towards organic halides which highly contrasts their behaviour towards other halides. However, carbon-carbon coupling reactions occur with Grignard reagents acting as a reactant when a metal catalyst is introduced.
- An example of such a coupling reaction is the reaction between methyl p-chlorobenzoate and nonyl magnesium bromide which yields the compound p-nonyl benzoic acid in the presence of the catalyst – Tris(acetylaceto) iron(III).

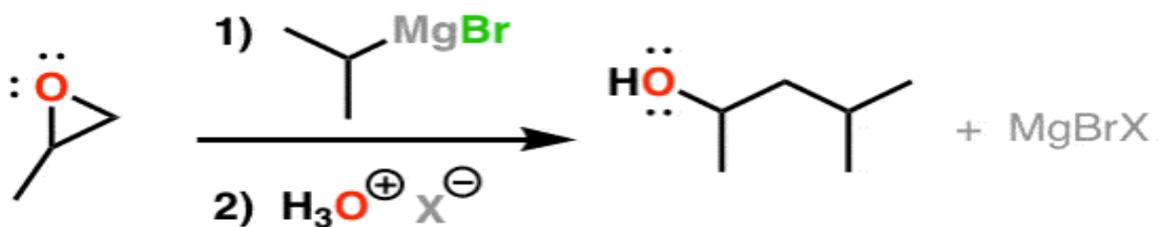
Reaction between Acetone and Methyl Magnesium Chloride

- The reaction of methyl magnesium bromide with acetone followed by hydrolysis gives tertiary alcohol.



Addition Of Grignard Reagents To Epoxides

Another important reaction of Grignard reagents is that they will add to epoxides to form carbon-carbon bonds. One thing to keep in mind here is that the tendency is for them to add to the **less** substituted end of the epoxide – that is, the less sterically hindered end.



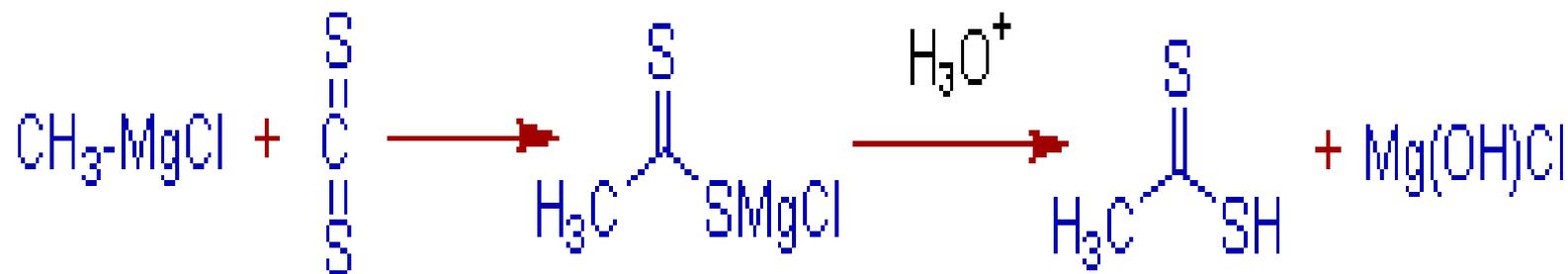
Grignard reagents add to the less substituted end of epoxides

The Grignard reagents react with **carbon dioxide** to give carboxylic acids.

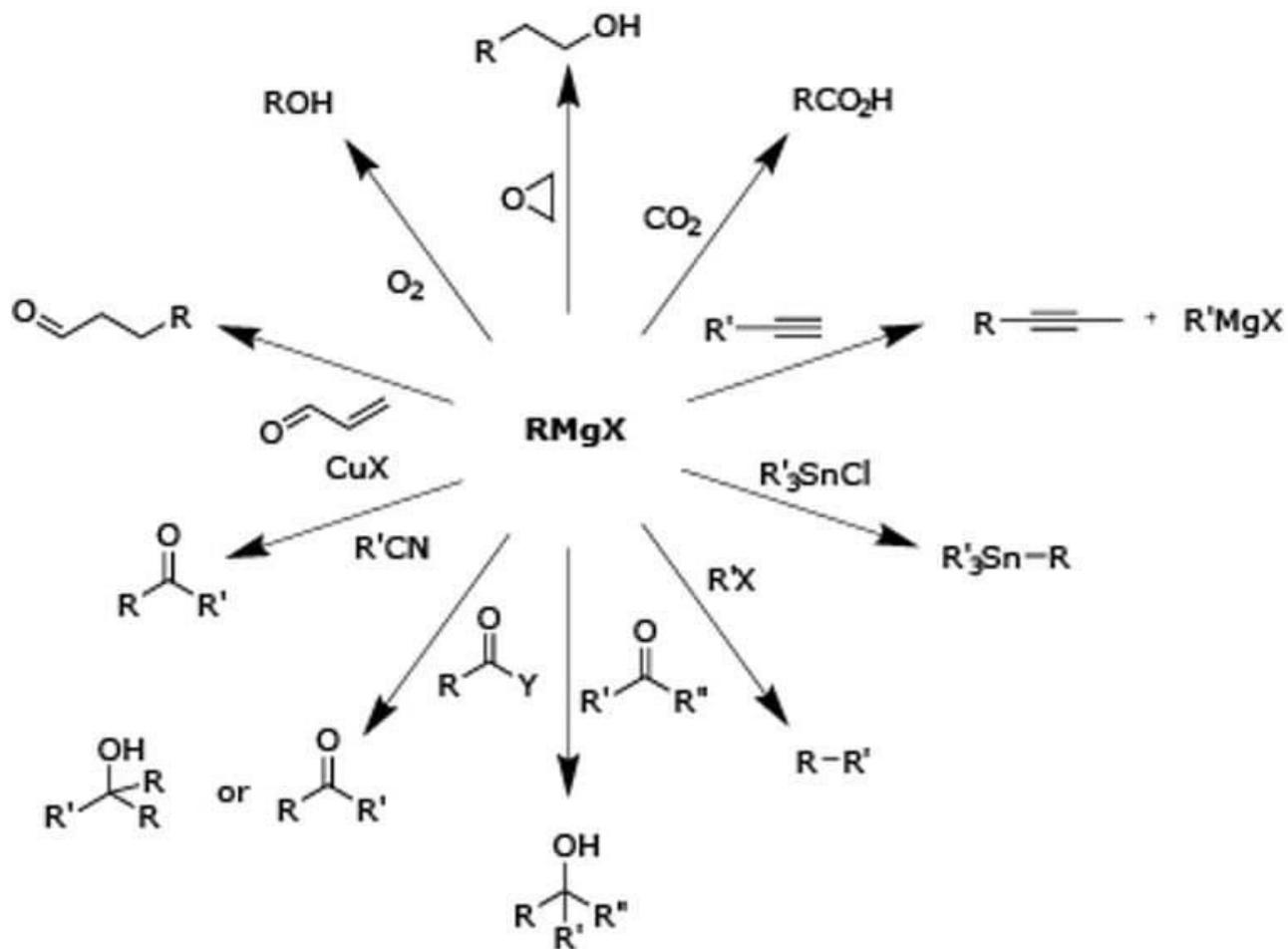
E.g. Methylmagnesium chloride gives acetic acid when reacted with carbon dioxide.



Ethanedithionic acid can be prepared by reacting methylmagnesium chloride with carbon disulphide, CS₂.



Reactions of Grignard Reagents



**THANK
YOU**

Department of Chemistry

Govt Dr Shyama Prasad Mukharjee Science and Commerce
College [Old Benazeer College]

Topic:- Nucleophilic substitution reactions

Presented By

Dr.Sudhanshu dhar Dwivedi

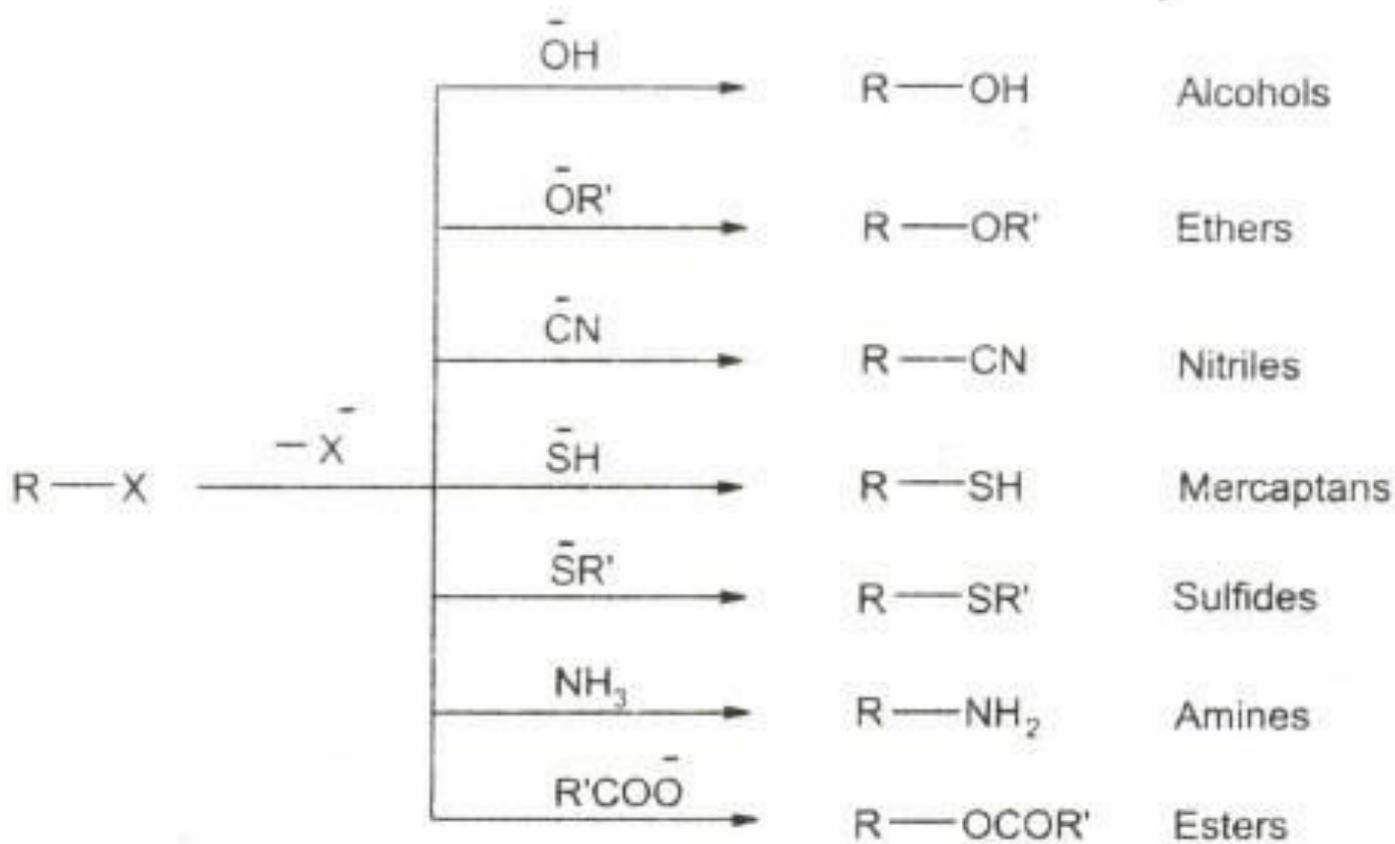
Nucleophilic substitution at saturated carbon atom

The replacement of one group by another is called substitution reaction. There are three main types of these reactions: radical, electrophilic and nucleophilic substitution. In this section we will deal with nucleophilic substitution at saturated carbon atom.

Attack of a nucleophile at a saturated carbon atom bearing a substituent, known as leaving group, results in substitution reaction. The group that is displaced (leaving group) carries its bonding electrons. The new bond is formed between nucleophile and the carbon using the electrons supplied by the nucleophilic reagent.



This is exemplified by the displacement of halogen atom with a hydroxide ion in the conversion of alkyl halide into an alcohol. Alkyl halides undergo substitution reactions with a variety of different nucleophilic reagents and are extremely important synthetically, as can be seen by the wide variety of compounds which can be prepared by its applications. The halogen is lost as a halide ion.



The compound on which substitution takes place is called the **substrate** and the group that becomes displaced from carbon, taking the electron pair with it, is called **leaving group**. The leaving group often leaves as an anion but may also be a neutral molecule. The substrate consists of two parts, alkyl group and leaving group. For example, reaction of methyl bromide with sodium hydroxide affords methanol and sodium bromide. In this reaction methyl bromide is substrate, bromide is leaving group and hydroxide ion is the nucleophile.



Nucleophilic substitution reactions have been studied extensively from a mechanistic viewpoint. Many factors influence the course of nucleophilic substitution reactions, including the nature of the nucleophile, its strength and concentration, the solvent, the nature of substrate, and the nature of leaving group.

Substitution reactions at saturated carbon can be mechanistically categorized as unimolecular (S_N1) or bimolecular (S_N2).

S_N1 (Substitution Nucleophilic Unimolecular)

An S_N1 reaction proceeds in two steps. The first step (slow step) is the rate determining step and involves the ionization of the reactant to form a carbocation intermediate. The breaking of C-X bond in RX takes place in a heterolytic fashion, in which both the bonding electrons go to the leaving group. In the second step (fast step), the intermediate carbocation is attacked by the nucleophile to give the final product.

Step 1. Formation of carbocation



Step 2. Capture of the carbocation by the nucleophile



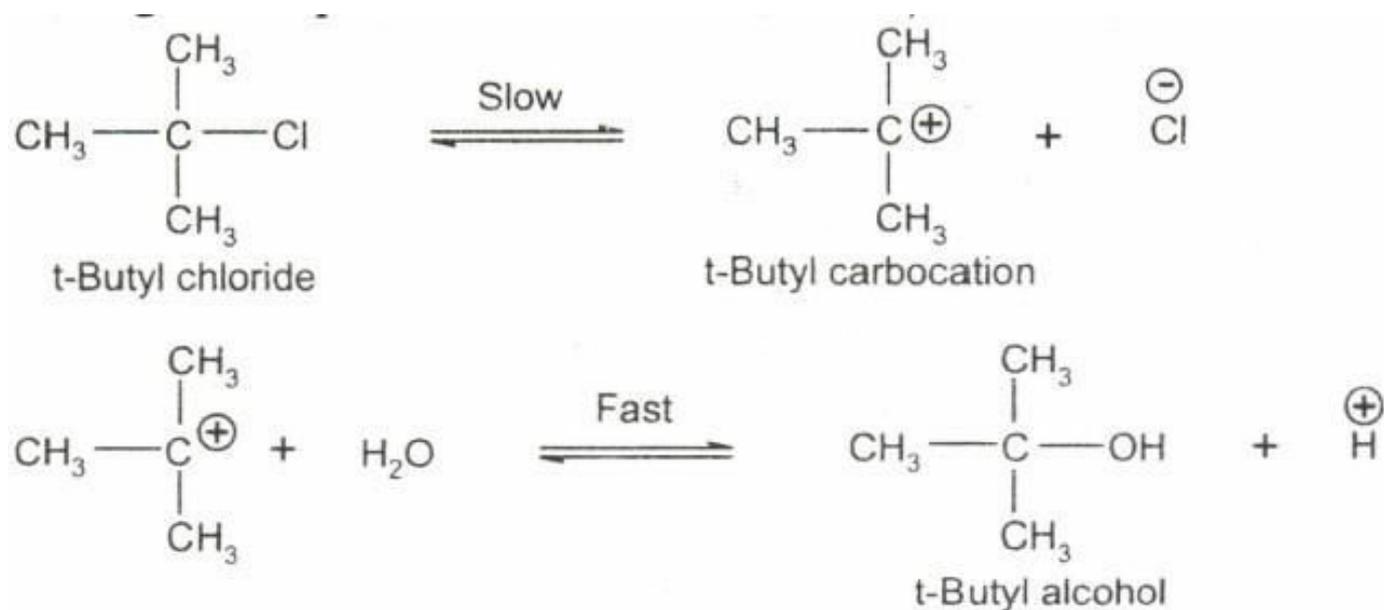
The S_N1 reaction shows first-order kinetics as rate of the reaction depends only on the concentration of the substrate (RX) and does not depend on the concentration of the nucleophile reacting with it. The rate expression is therefore:

$$\text{Rate} = k[\text{RX}]$$

where k is rate constant and quantity in square brackets represents concentration.

In several reactions, nucleophile is a solvent molecule such as water, ammonia or alcohol such substitution reactions are called solvolysis.

For example, hydrolysis of tert-butyl chloride to tert-butyl alcohol follows S_N1 process. In the first step, tert-butyl chloride ionizes to a tert-butyl carbocation, which is captured in a second step by the nucleophilic solvent, water, to give the protonated alcohol first and then alcohol itself.



An energy diagram (Following figure) for S_N1 reaction involves two transition states. The transition state for the slow step (the ionization step) is higher in energy than the transition state for the fast step (second step, the capture of the ion by a nucleophile).

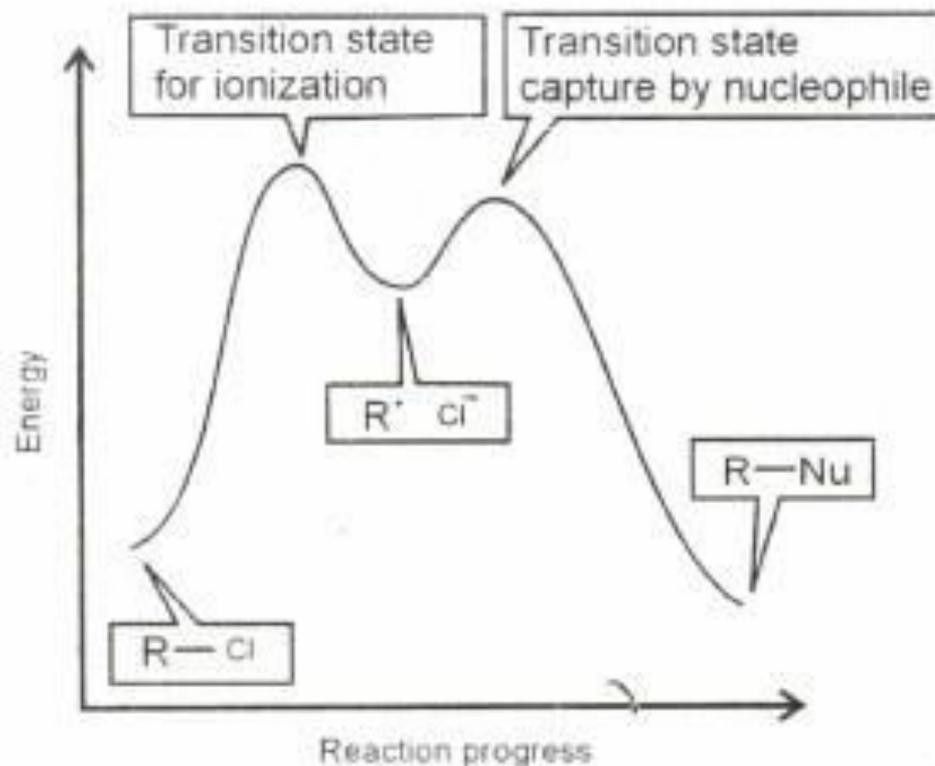
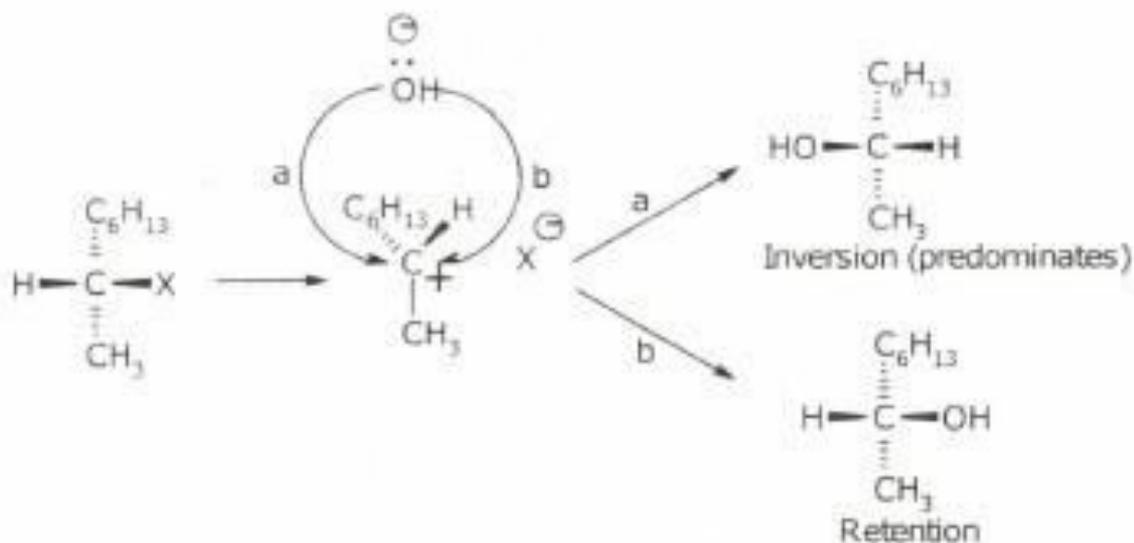


Fig. 1.6 : An energy diagram for the S_N1 reaction. Notice that the transition state for the slow step in the reaction, the ionization is higher in energy than the transition state for the capture of the ion by a nucleophile

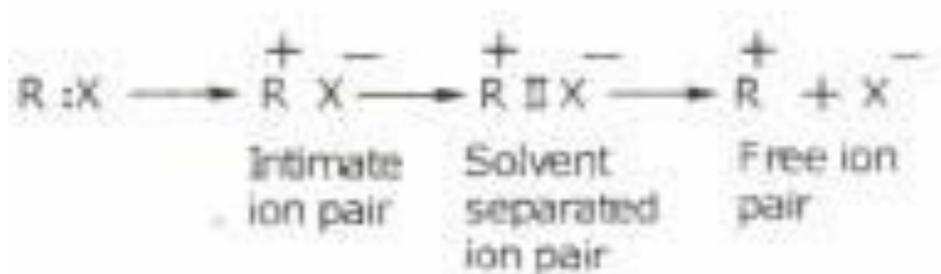
Stereochemistry of the S_N1 reaction

Ionization of optically pure alkyl halide molecule leads to the planar, achiral (symmetrical) carbocation with an empty p-orbital perpendicular to the plane. Addition of nucleophile can take place at both sides of the carbocation with equal ease owing to the symmetry of carbocation, resulting in a racemic mixture (equal amounts of R and S products). But in actual practice, depending on the nature of substrate, solvent and leaving group, there may be a preferred side for its attack by nucleophile, in which case the product will contain unequal amounts of the two enantiomers, yielding partially optically active product.



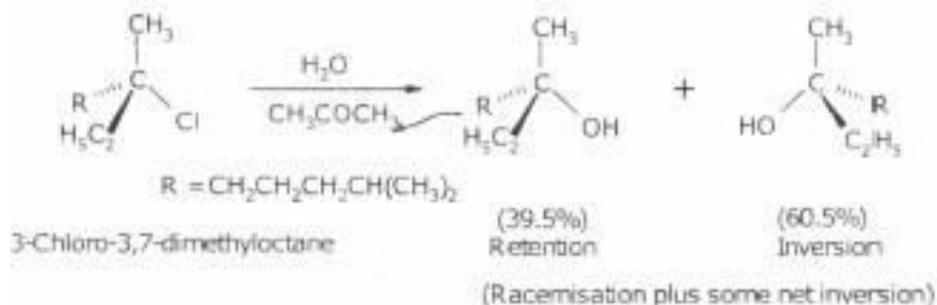
S_N1 reaction leads to racemization plus inversion

It is believed that carbocation and leaving group exist for a while as an intimate ion pair and the attack of nucleophile during this time takes place only on the back side of carbocation, but not on the front side, giving rise to inversion. Then these ions diffuse apart as solvent intervenes, and become free ions. Now attack of nucleophile on free symmetrical carbocation occurs from the back side or from the front side with equal probability.

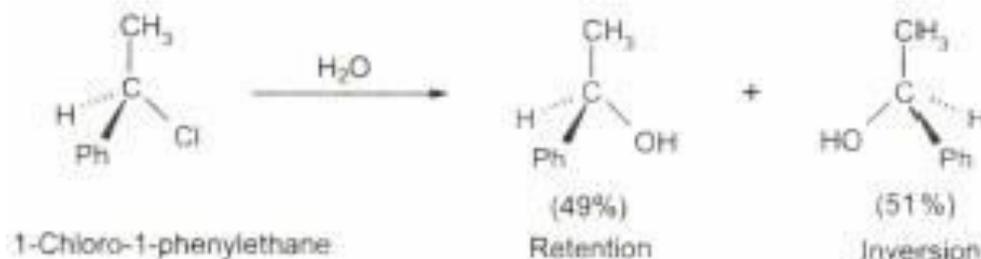


If the carbocation is less stable, it is more likely to be attacked by nucleophile before leaving group separates from it, giving rise to inversion. Thus in this case the reaction proceeds with racemisation plus some net inversion.

For example, when 3-chloro-3,7-dimethyloctane is hydrolyzed in presence of acetone, there is a 21% excess of the product resulting from inversion of configuration.



However, if the carbocation is stable enough to survive the attack of nucleophile during the ion pair stage, the observed product becomes completely racemized. For example, hydrolysis of 1-chloro-1-phenylethane occurs with extensive racemization (98%) and only 2% inversion. 1-Chloro-1-phenylethane ionizes to give benzylic carbocation which is stabilized because of resonance and the ions can diffuse apart before nucleophile attacks the carbocation. Now reaction of free carbocation with nucleophile can take place from both sides of the cation to give the 51% inverted alcohol and 49% alcohol with retention of configuration (98% racemization and 2% net inversion).



Thus, we can interpret these facts to mean that the S_N1 mechanism proceeds *via* an intermediate carbocation that is not completely free to react with nucleophile on both sides. The leaving group is still close enough to shield the side of the carbon atom of carbocation for some time to which it was attached from nucleophilic attack. The result is usually an excess of inversion in most S_N1 reactions.

Effect of solvent

The solvent plays an important role in S_N1 reactions as the energy required to effect the initial ionization is largely recovered from the energy evolved through solvation of the resulting ion pair. The S_N1 process requires the ionization of a covalent bond which is encouraged by solvents with high dielectric constants. There is a greater charge on the intermediate ions than that on starting substrate as majority of the substrates are neutral. Polar protic solvent (such as water or alcohol) will thus solvate and stabilize the intermediate ions more than it does the reactant. Since ions are usually formed in the rate determining step (slow step) of the reaction, therefore the S_N1 reaction will usually be favoured by a polar protic solvent. Good solvents for S_N1 displacements almost always contain hydroxyl groups (as in water, alcohols, or carboxylic acids) because the electronegative oxygen atom interacts with the incipient positive charge, and the electropositive hydrogen atom (through hydrogen bonding) interacts with the incipient negative charge. Thus, in addition to dielectric constant, the ability to form hydrogen bond with X - makes a protic solvent the better solvent than aprotic solvent which cannot form hydrogen bond. The S_N1 process occurs mainly when water is present as a solvent or as a co-solvent.

Effect of nucleophile on rate

The rate of S_N1 reaction is independent of the nucleophile. A better nucleophile will not accelerate the S_N1 reaction, and yet it may determine which product is formed. For example, t-butyl bromide in water containing small amount of cyanide ions gives t-butyl cyanide. This is because the cyanide is many times more reactive towards carbocations than the water. Weak nucleophiles with low concentrations favor the S_N1 mechanism.

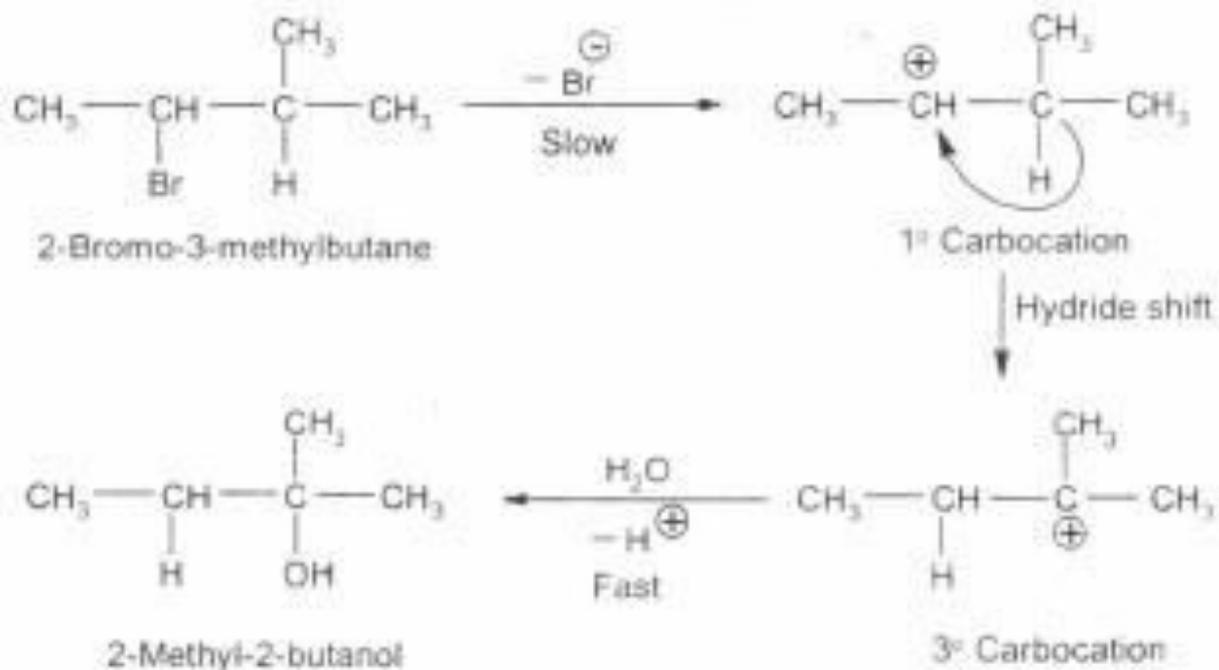
Effect of leaving group on rate

The rate of S_N1 reaction is largely influenced by the nature of the leaving group. The rate of ionization is affected by the stability of the leaving group, X^- . The more stable the leaving group, the more easily it will be lost. S_N1 reactions therefore are favored by the presence of good leaving group such as sulfonates (tosylate or mesylate).

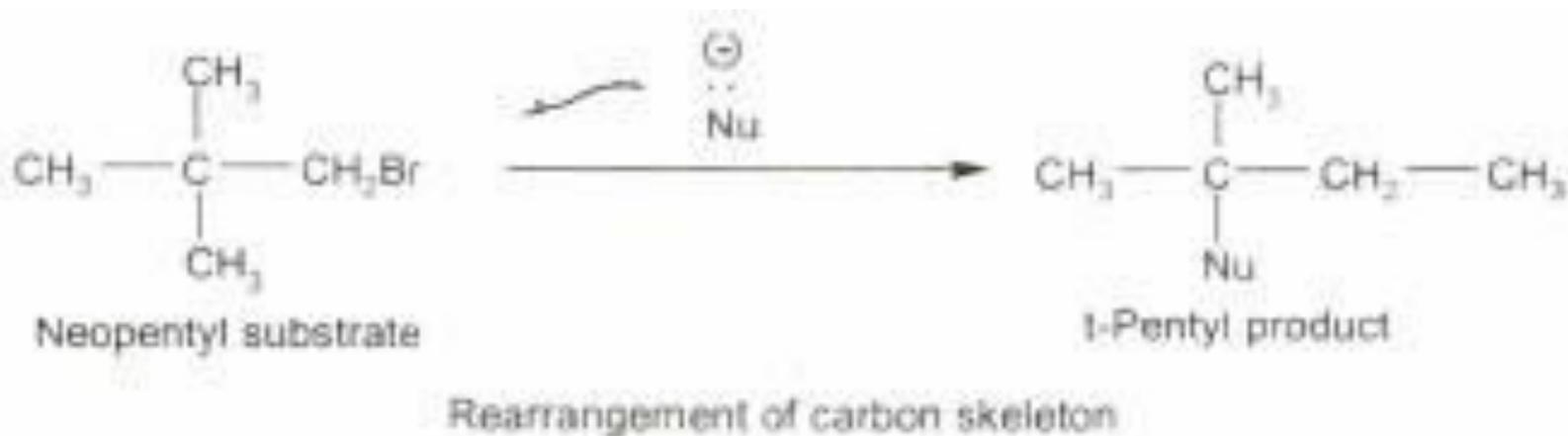
The weaker the Bronsted basicity of X^- , the better leaving group is X . In case of halides the order of basicity is : $I^- < Br^- < Cl^- \ll F^-$, therefore, iodide is a better leaving group than bromide and bromide is a better leaving group than chloride. Presence of acid catalysts or metal ions sometimes favour the departure of the leaving group, e.g., silver ions aid the departure of halide ion from alkyl halides.

Rearrangement in S_N1 reactions

The evidence for the formation of carbocations is that they undergo reactions other than simple addition to nucleophiles. For example, carbocations may rearrange before combining with nucleophiles. Since S_N1 mechanism involves carbocation intermediate, therefore, unexpected products are also formed. For example, hydrolysis of 2-bromo-3-methylbutane yields 2-methyl-2-butanol.



We see that in S_N1 reactions, a carbocation is formed by loss of the leaving group from the substrate. If a 1,2-shift of hydrogen can form a more stable carbocation, then such a rearrangement takes place. The rearranged carbocation can react with nucleophile to afford the substitution product or it may lose a proton to yield an alkene. If the intermediate carbocation can rearrange to a more stable carbocation *via* 1,2-alkyl shift, the reaction often proceeds with rearrangement of the carbon skeleton of the organic substrate.

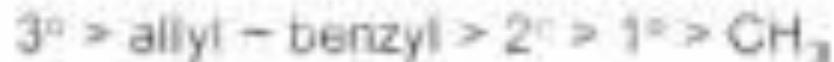


Effect of the nature of substrate on the rate

The rate determining step is the formation of planar carbocation in S_N1 process. Therefore, the order of reactivity among organic substrates will depend upon the stability of carbocation formed after ionization of substrate. Hence tertiary alkyl halides, which give rise to tertiary carbocations, react faster than secondary ones, which react faster than primary halides.

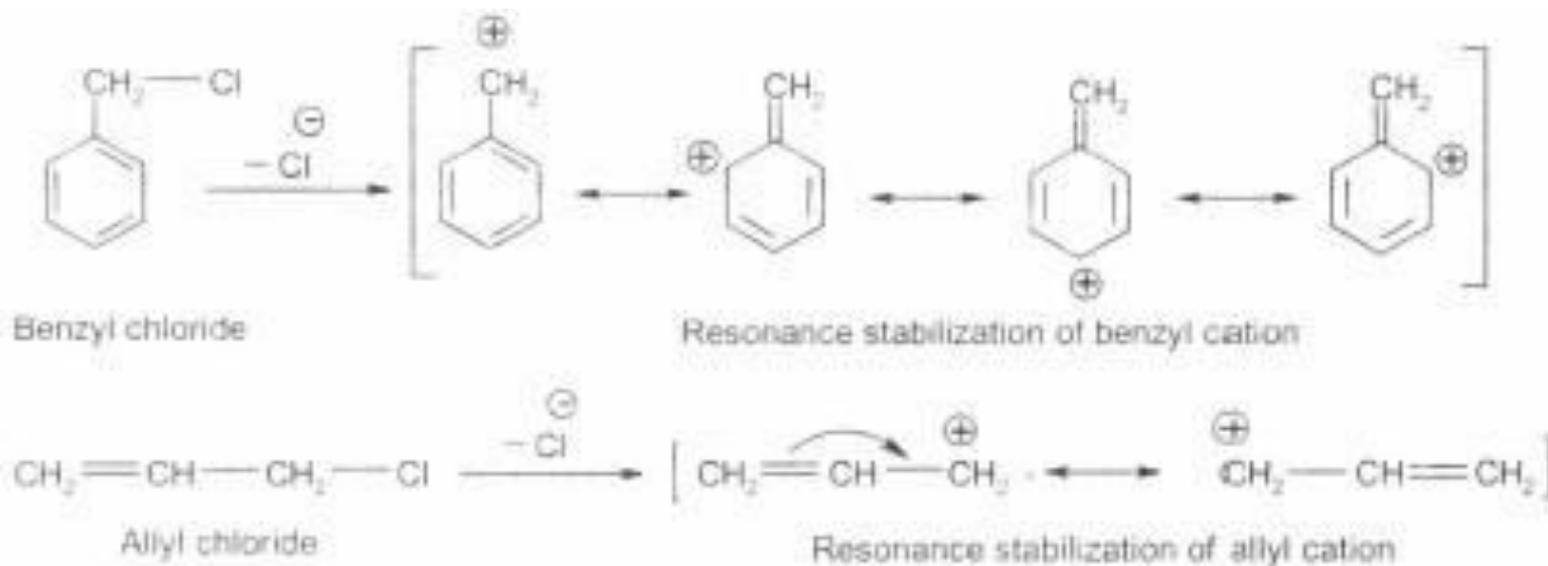
The introduction of a methyl group in place of a hydrogen atom attached to the positive carbon of a carbocation appears to stabilize the ion by 15 to 30 kcal / mol (through inductive and hyperconjugation effects). In most of the cases, the substituents which have +I and or +M effects, stabilize the carbocations. Allylic, benzylic, and tert-carbocations are relatively stable carbocations, therefore, allylic, benzylic and tert-halides can react by an S_N1 mechanism.

Stability of carbocations

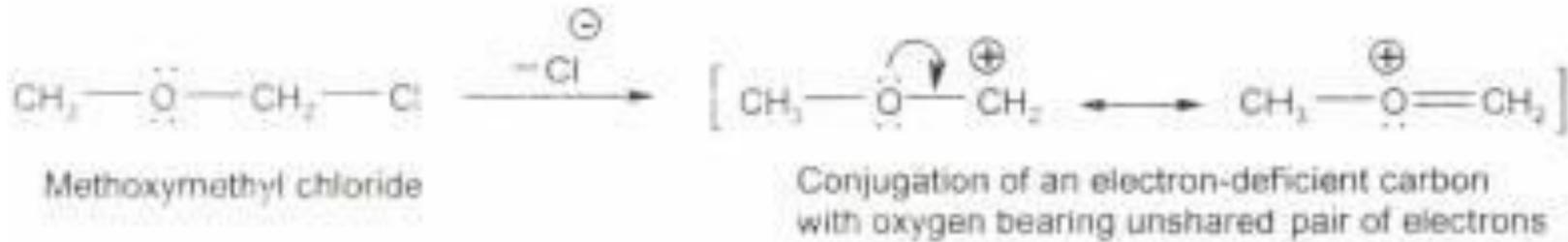


Both benzyl and allyl carbocations disperse the charge by resonance and are more stable than primary alkyl or secondary alkyl carbocations. The primary alkyl and methyl halides, which would form extremely unstable carbocations, do not generally react by the S_N1 process. The order of reactivity among organic halides is as follows:

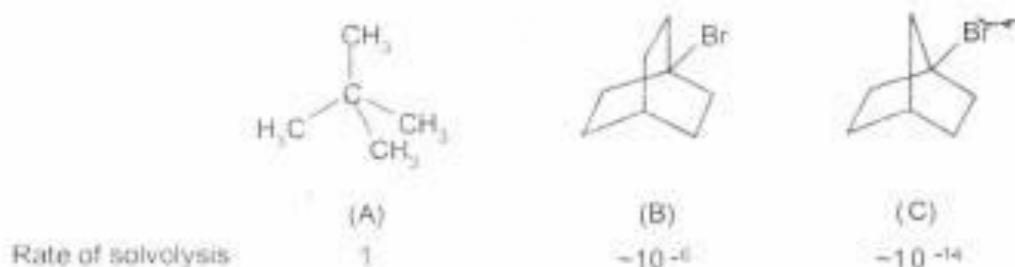
t-alkyl halides > allyl halides ~ benzyl halides > s-alkyl halides > 1°-alkyl halides



Methoxymethyl chloride undergoes hydrolysis more than 10^4 times faster than methyl chloride. This is because, the carbocation formed after ionization of methoxymethyl chloride is resonance stabilized. The $\text{CH}_3\text{O}-$ group has unshared pairs of electrons that it tends to share, thus acquiring a positive charge.

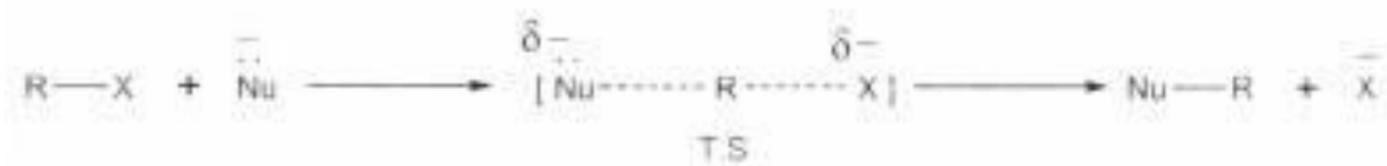


S_N1 displacement in bridged bicyclic compounds at bridgeheads is very slow or does not take place. This is expected as a flat (planar) intermediate carbocation can not be formed at the bridgehead carbon because of the rigid framework of bicyclic systems. Greater is the rigidity about the bridgehead carbon, lower will be its reactivity. For instance, rate of solvolysis of compounds A, B and C in 80% aqueous ethanol at 25°C decreases as the rigidity about the bridgehead carbon increases ($A < B < C$).



S_N2 (Substitution Nucleophilic Bimolecular)

S_N2 process proceeds in one step *via* a transition state. The nucleophile attacks the substrate carbon simultaneously pushing out the leaving group in a concerted fashion.



The reaction between methyl iodide and hydroxide ion is an example of the S_N2 mechanism. Kinetic evidence shows that the rate of this reaction is proportional to both the concentrations of substrate and nucleophile. Thus, S_N2 reactions follow second-order kinetics and is described by the rate expression:

$$\text{rate} = k [\text{RX}] [\text{Nu}]$$

where k is rate constant and quantities in square brackets represent concentrations.

In S_N2 process there is synchronous attack by the nucleophile from the opposite side of the carbon atom of substrate bearing the leaving group, such that C-X bond of the substrate breaks only as the new C-Nu bond of the product is forming. Therefore, in transition state, the nucleophile-carbon bond is partially formed and the C-X bond is partially broken. The approach of the nucleophile from the side of the molecule bearing the leaving group is **unfavorable** due to electrostatic repulsion and also due to steric factors. In the transition state for this reaction, the three non reacting substituents on carbon lie in a plane with the carbon undergoing reaction. This plane is between the incoming and outgoing groups.

An energy diagram (Following figure) for S_N2 process shows the reactants being converted to products by way of **one transition state**, with no energy minimum representing a reactive intermediate. The reactants and products are separated by the high energy point of the reaction, the transition state. The energy difference between the reactants and transition state is called the activation energy and is related to the rate of reaction. Higher the activation energy, slower the reaction. The reactants and products are not at the same energy level therefore, the forward reaction is exothermic reaction, as read from left to right and backward reaction is endothermic, as read from right to left.

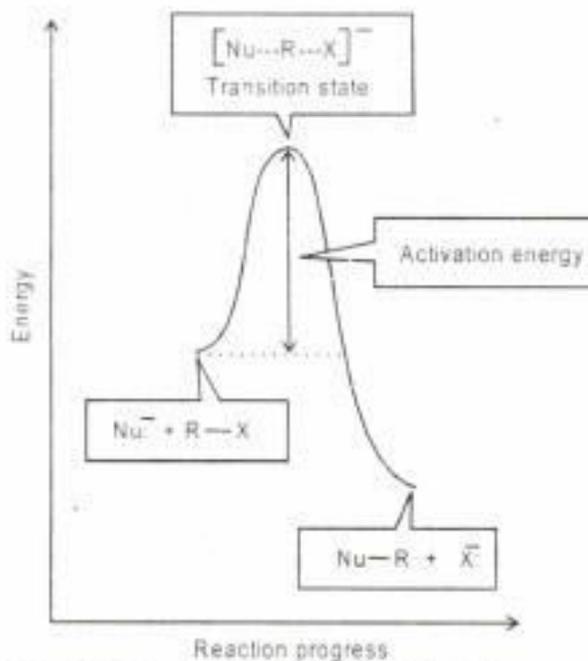
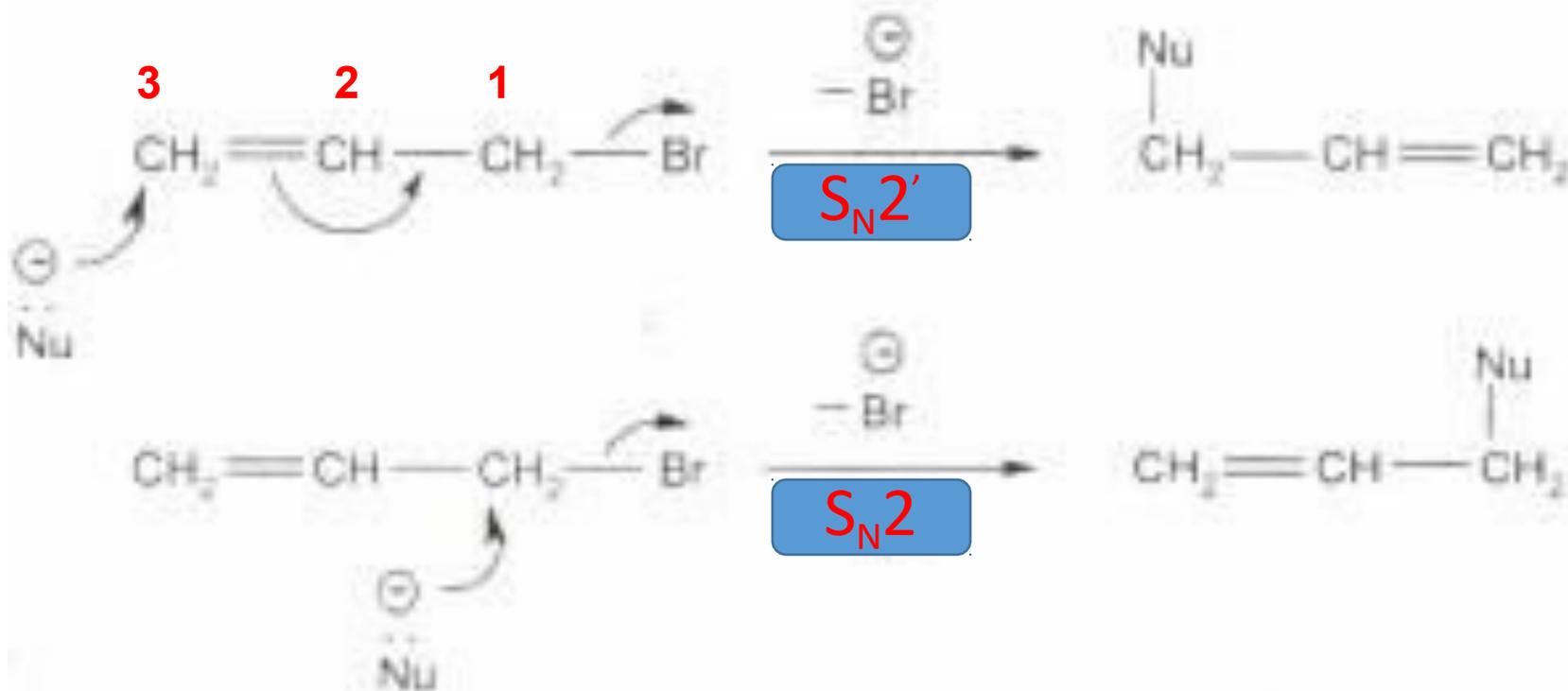


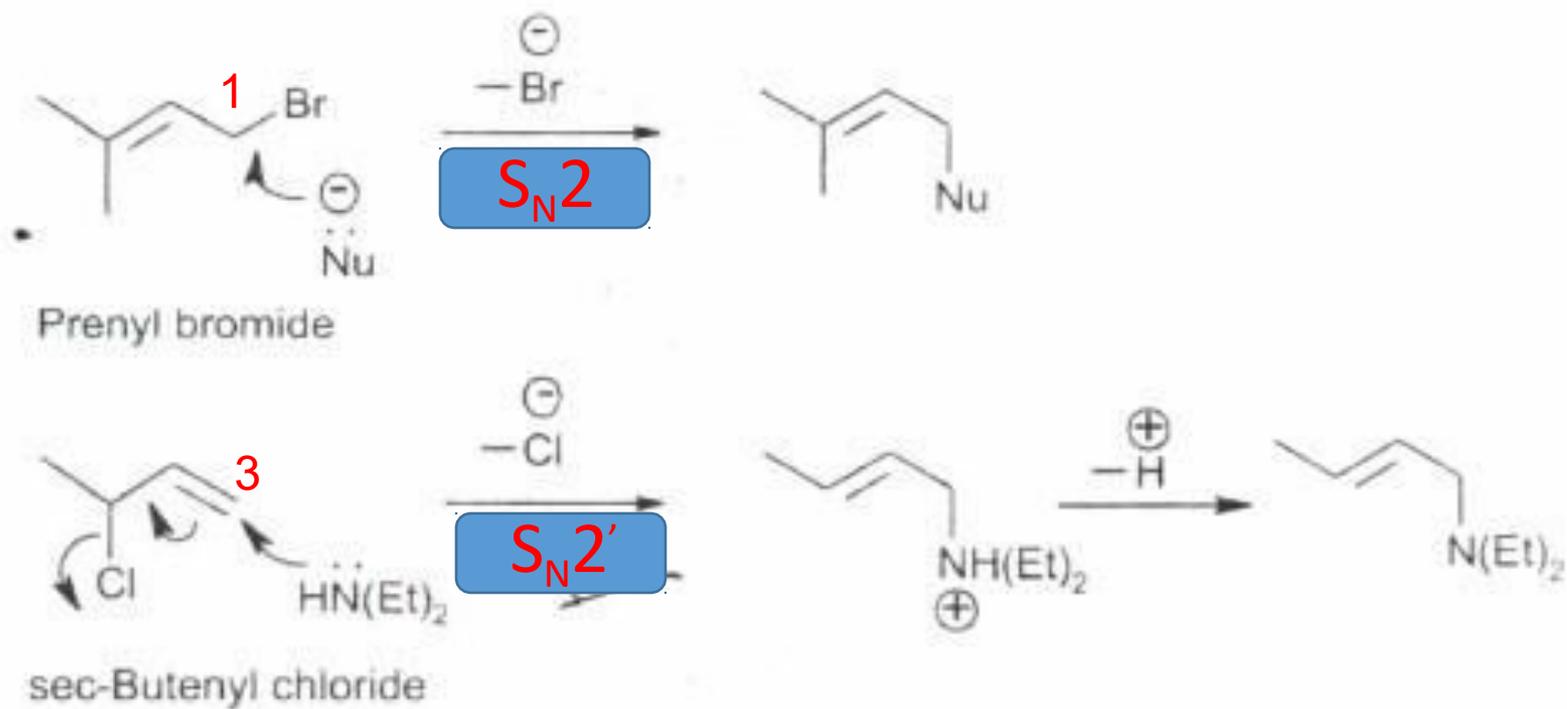
Fig. 1.7 : An energy diagram for the S_N2 reaction.

Rearrangement in S_N2

Since no free carbocation is generated, therefore, S_N2 displacement afford unrearranged products. However, **some times S_N2 reaction, leads to allylic rearrangement.** The attack of nucleophile takes place at the end of the π -system i.e. on C-3 of the allylic-system, with simultaneous expulsion of a leaving group. Such reactions are **referred to as S_N2'** , to distinguish them from the normal S_N2 process.

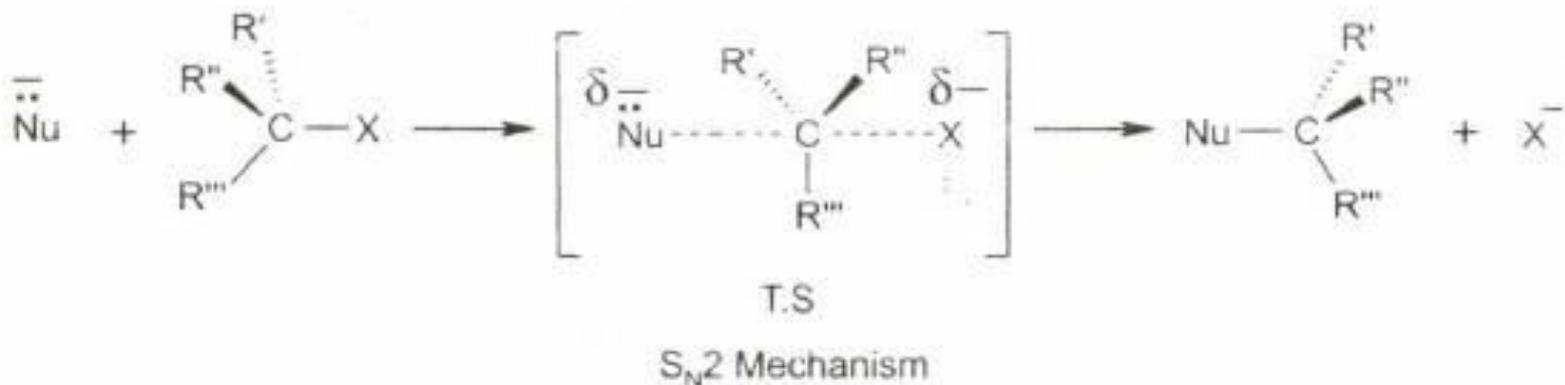


S_N2' mechanism leads to the same product as S_N2 , **however, if the allylic halide is unsymmetrically substituted**, we can tell which mechanism operates and the product formed will be from the nucleophilic attack at the less hindered end of the allylic system. Prenyl bromide, for example, reacts entirely *via* S_N2 process. If we react the secondary butenyl chloride with an amine we get the product from S_N2' mechanism

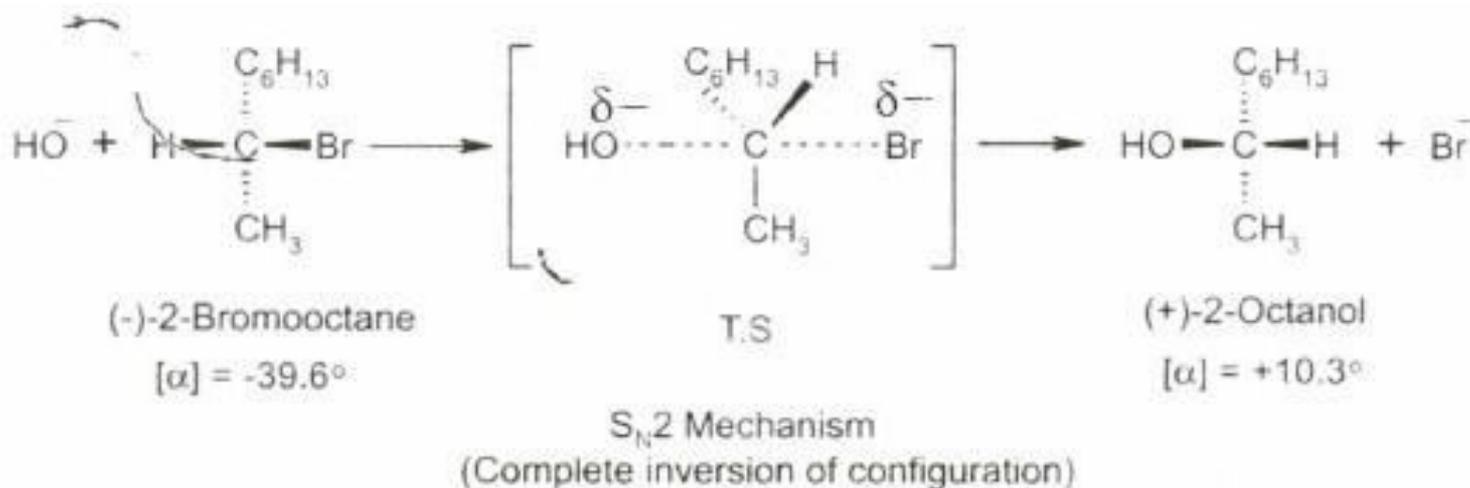


Stereochemistry of S_N2 reaction

Most of the S_N2 reactions proceed with **complete inversion** of configuration of the substrate. The observation of inversion in S_N2 reaction means that the nucleophile (incoming group) must be approaching the substrate from the side opposite (back-side) to the group being displaced (leaving group). Such an attack will flip the other three groups from one side of the carbon atom to the other. This process is known as **Walden inversion** and produces a product of the opposite configuration.

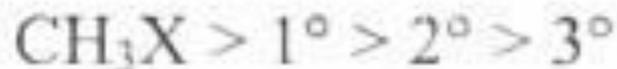


For example, when optically active substrate, (-)-2-bromooctane reacts with sodium hydroxide under conditions where S_N2 mechanism are followed, inversion of configuration is observed.



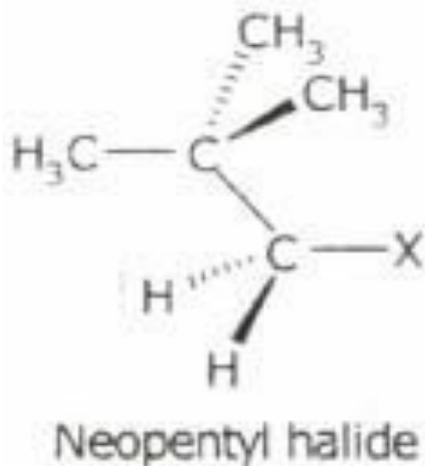
Effect of the nature of substrate on rate

The steric hindrance around the carbon site makes a huge difference in the rate of the S_N2 reaction. The central carbon atom in reactant and product is tetrahedral, whereas carbon in the transition state is bonded to five atoms or groups therefore, there will be an increase in crowding on going from the starting substrate to the transition state. A transition state with five groups crowded around the central carbon atom is a high-energy transition state. The more crowded the transition state relative to substrate, the higher its energy will be, and the slower it will be formed. As hydrogen atoms are replaced by the larger methyl groups, there is increased crowding about the carbon. Therefore, the methyl compounds react faster than primary substrates and primary substrates react faster than the secondary substrates. Tertiary substrates have three bulky alkyl groups attached to reaction center which hinder the approach of the entering nucleophile. Thus, tertiary alkyl halides such as t-butyl bromide normally do not undergo substitution *via* this mechanism. The reactivity of substrates in S_N2 reactions is:



This order is the reverse of that in S_N1 reactions.

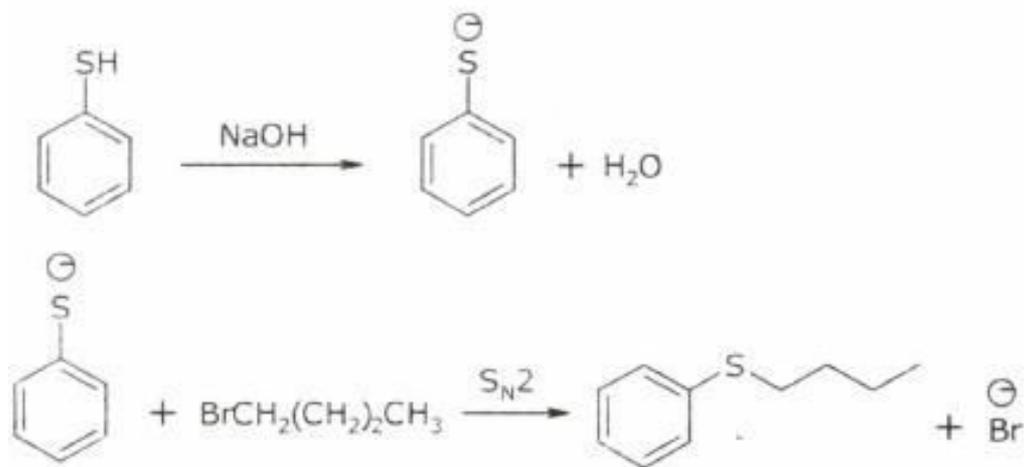
Even though the site of reaction in neopentyl derivatives is primary, the t-butyl group is large enough to slow down the bimolecular (S_N2) displacement.



In allyl and benzyl halides, the π -bond assists in expelling the leaving group, and both halides react faster than the alkyl halides.

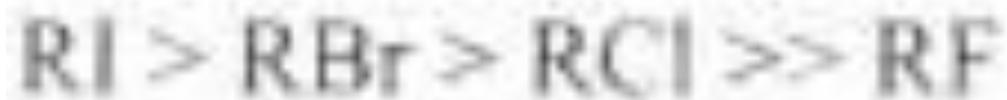
Effect of the nucleophile

The rate of S_N2 reaction is strongly dependent on the nature of nucleophilic reagent used, it increases with the nucleophilic strength of the incoming nucleophile. Thus, with the change of nucleophile a shift in mechanistic type may occur, for example, the mechanism which is S_N1 with water may become S_N2 with hydroxide ion. Sulfur nucleophiles are better than oxygen nucleophiles in S_N2 reactions. For example, thiolate anions (excellent nucleophiles in S_N2 reactions) react with alkyl halides to give good yield of the sulfide as illustrated by the following reaction.



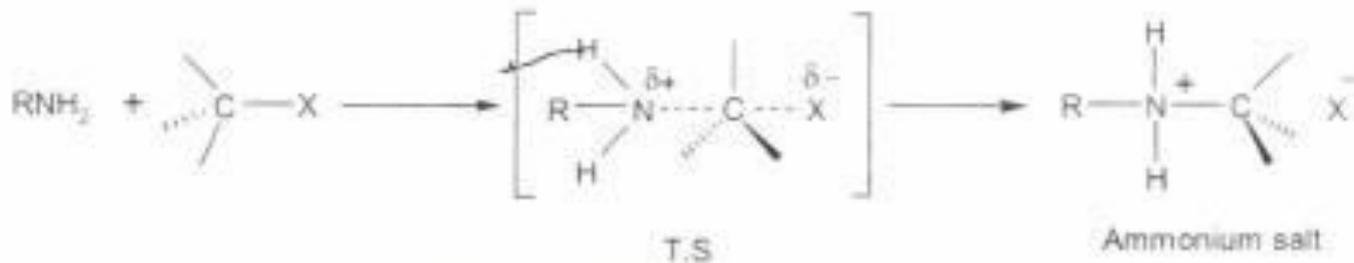
Effect of the leaving group

Weak base of strong acid is best leaving group, thus, the rate of S_N2 reaction (same as for S_N1) is higher if the leaving group is a stable ion and a weak base. In case of alkyl halides the order of reactivity is:



Effect of solvent

Normally, S_N2 process involving reaction of anionic nucleophiles with the alkyl halides is suppressed in the presence of polar protic solvent (such as water), since a polar protic solvent will interact (through hydrogen bonding) more favorably with anionic nucleophiles than with the transition state. Therefore, polar protic solvents slow down the reaction, and polar aprotic solvents are preferred for S_N2 reactions. Polar protic solvents can solvate ionic reagents (both the cations and anions), as a result, the anion is "caged" by the solvent molecules. This stabilizes the anion, and makes it less reactive. Thus, S_N2 mechanism becomes less important. However, polar aprotic solvents are not able to form hydrogen bonding with anionic nucleophiles, as a result, nucleophiles are "free" and more reactive. However, if both substrate and nucleophile are neutral but the product is charged, as in the substitution by amines or phosphines on an alkyl halide, the polar protic solvent will solvate and separate the developing charge in the transition state, ultimately accelerating the S_N2 process.



(Solvation and ion separation by polar protic solvent will accelerate the S_N2 process)

Competition between S_N1 and S_N2

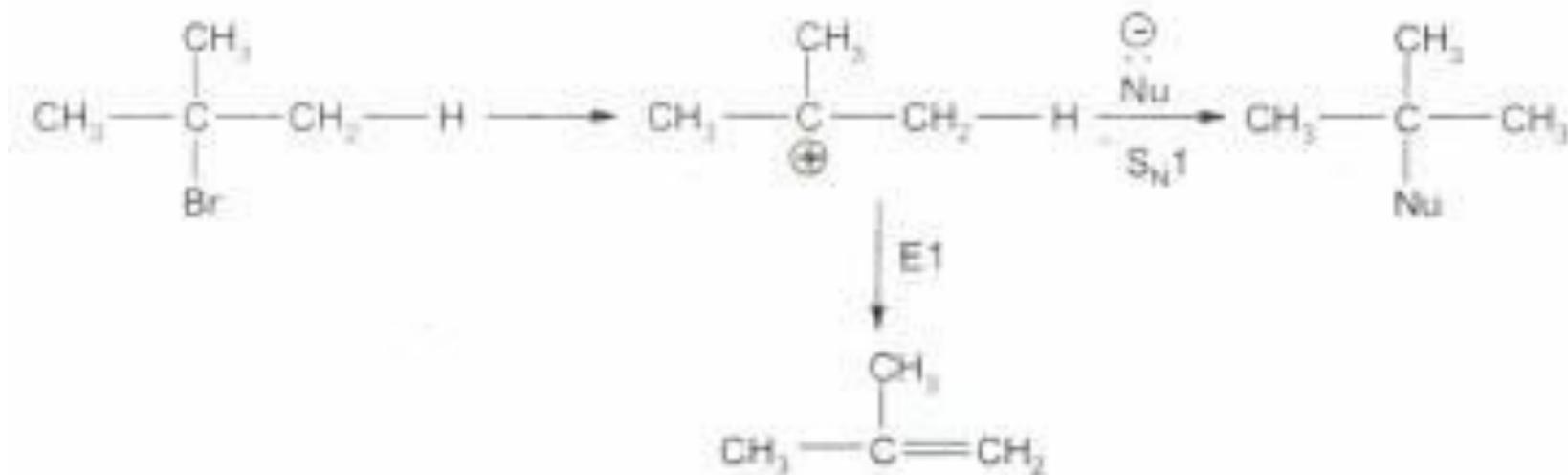
The structure of substrate, the nature of the nucleophilic reagent, polarity of solvent, and other experimental conditions determine whether nucleophilic substitution will take place by S_N1 or by S_N2 mechanism. In general, primary halides undergo substitution by S_N2 mechanism and tertiary halides undergo substitution by S_N1 mechanism. Secondary halides may undergo substitution by both S_N1 and S_N2 mechanisms, however, one mechanism may be maximized by the selection of appropriate conditions. High concentration of the nucleophile and / or presence of strong nucleophile favors S_N2 , while the factors promoting the S_N1 are, lower concentration of nucleophile or the absence of strong nucleophile, solvents of great ionizing power (such as water) and substrate leading to stable carbocations. The reaction rates of both the S_N1 and S_N2 reactions are increased if the leaving group is a stable ion and a weak base.

Competition between substitution reaction and elimination reaction

Besides undergoing substitution reaction, another common reaction of substrate is an elimination reaction where nucleophile acts as a base to remove HX instead of adding to the substrate. Elimination can therefore, compete with substitution. Many factors influence the extent of this competition, including the nature of nucleophile, its strength, the solvent and the substrate. The strong bulky Bronsted bases favor E_2 and strong nucleophiles favor S_N2 process. For instance, bulky tert-butoxide anion (Me_3CO^-) can abstract a proton from the periphery of the molecule but is hindered as a nucleophile. However, some anions such as thiol anion (RS^-) are less basic and more strongly nucleophilic.

The $E_2 : S_N2$ ratio increases with increased substitution by alkyl groups. Primary alkyl halides will usually undergo S_N2 substitution reaction in preference to E_2 elimination reaction. As base strength increases, the rate of competitive elimination will increase, but substitution reactions compete when the base is also a good nucleophile. Polar aprotic solvents are used to maximize the yield of S_N2 products and suppress side reactions such as elimination.

The E_1 and S_N1 involve the formation of the same intermediate, carbocation, by the same rate controlling ionization step. However, the course of the reaction can often be controlled by specific reaction conditions. A high concentration of nonbasic nucleophiles in aqueous media favors the unimolecular substitution (S_N1), whereas unimolecular elimination (E_1) processes are favored with bases of weak to moderate strength that are also poor nucleophiles. In general, unimolecular substitution is faster than unimolecular elimination, since the cationic carbon is more strongly attracted to the electron-rich center.

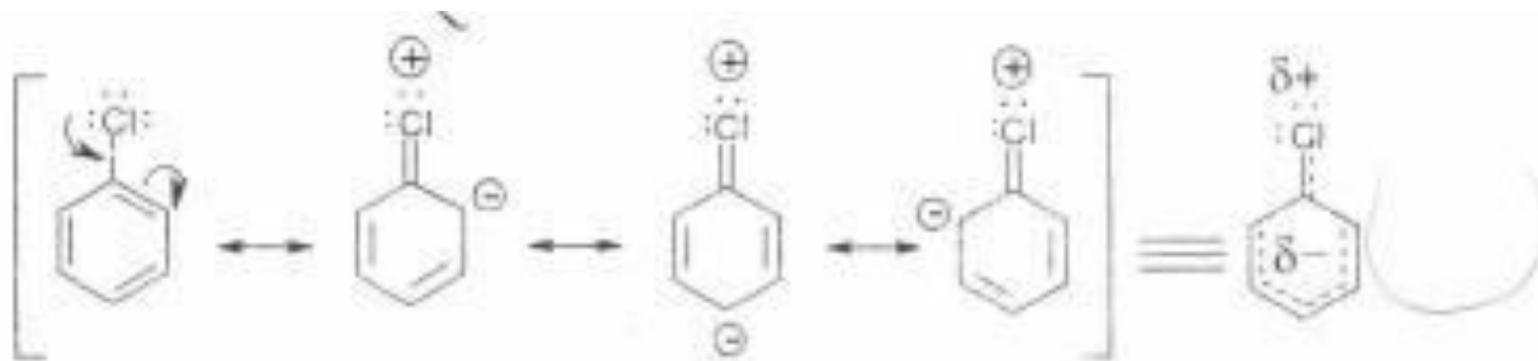


Low reactivity of vinyl and aryl halides

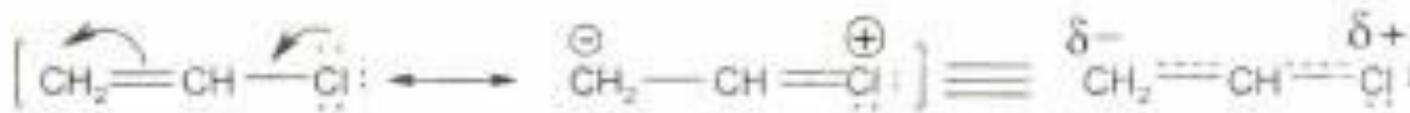
Halogen attached to a doubly bonded carbon or on aromatic nucleus is usually quite unreactive. The aryl halides show extremely low reactivity towards nucleophilic substitution reactions. They usually do not undergo nucleophilic substitution reactions unless electron-withdrawing groups are located *ortho* or *para* to the halogen on the aromatic ring. Similarly, vinyl halides are very much unreactive toward nucleophilic substitution reactions than their saturated counterparts.

The low reactivity of alkyl and vinyl halides is because of the fact that they contain shorter and stronger carbon-halogen bond. For example, in chlorobenzene and vinyl chloride the C-Cl bond length is 1.69\AA , as compared with a bond length of $1.77\text{-}1.80\text{\AA}$ in a large number of alkyl chlorides. This is attributed to the sp^2 hybridization of the carbon atom holding halogen. Since, carbon atom having sp^2 hybridization is more electronegative than sp^3 hybridized carbon atom, therefore, the carbocation intermediates formed by the ionization of aryl and vinyl halides are thermodynamically less stable than alkyl carbocations. This prevents the S_N1 mechanism from operating in aryl and vinyl halides.

The other reason for this unreactivity is that the π -orbital of the double bond overlaps with the p-orbitals of the halogen atom to form delocalized cloud of the π -electrons with the result that C-X bond attains a partial double bond character. The partial double bond character of the C-X bond results in strengthening of the bond and hence it is difficult to break as compared to single bond. Both of these effects inhibit nucleophilic substitution reactions of either the S_N1 or S_N2 type, thus net reactivity of the molecule is considerably less than that of saturated alkyl halides.



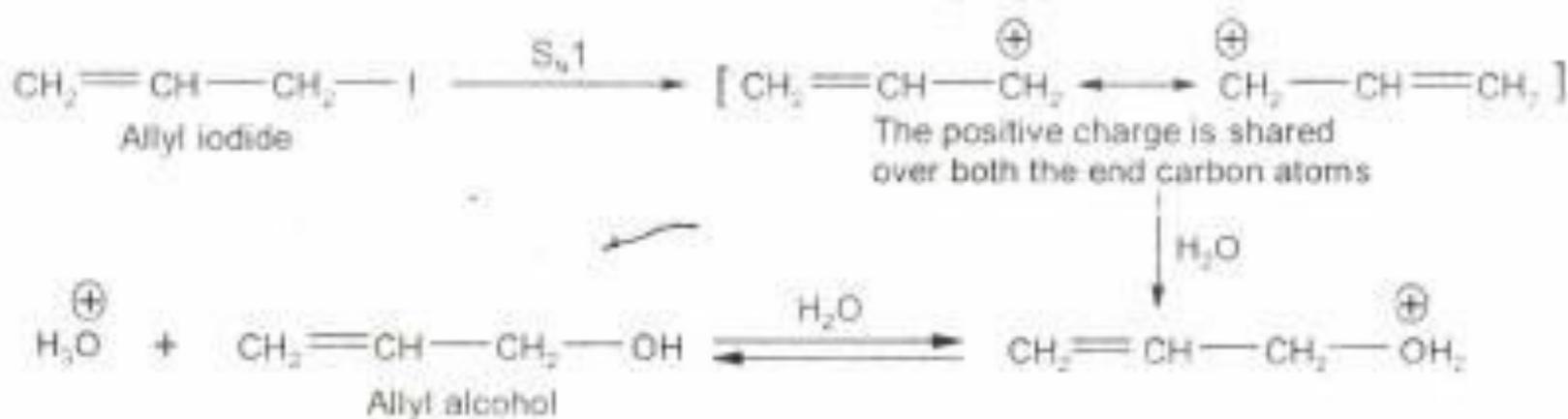
Delocalization of electrons by resonance in chlorobenzene



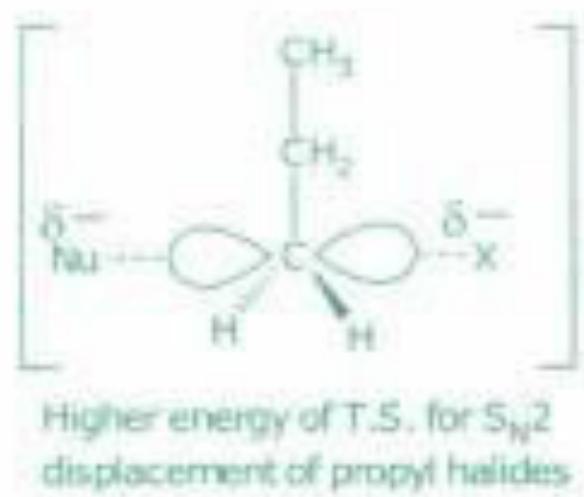
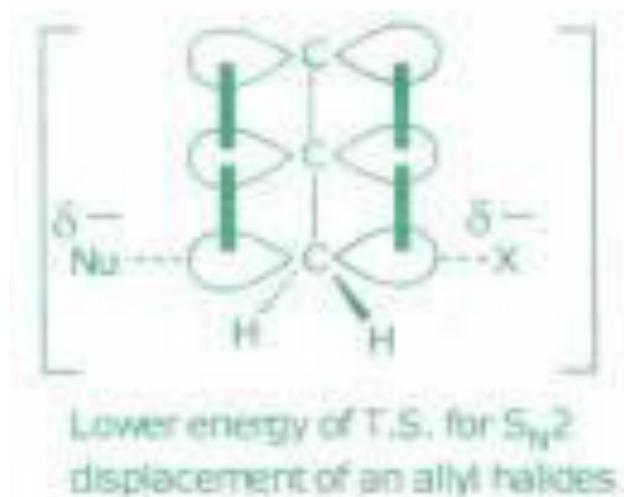
Delocalization of electrons by resonance in vinyl chloride

High reactivity of allyl and benzyl halides

On the other hand, allyl halides and benzyl halides are more reactive than saturated halides. Allyl and benzyl halides are especially reactive under S_N1 conditions because of the resonance stabilization of the intermediate allyl and benzylcarbocations, respectively. The resonance stabilization of intermediate carbocations has an acceleration effect on the ionization of allyl and benzyl halides. For example, solvolysis of allyl iodide in water proceeds much faster than the solvolysis of propyl iodide.

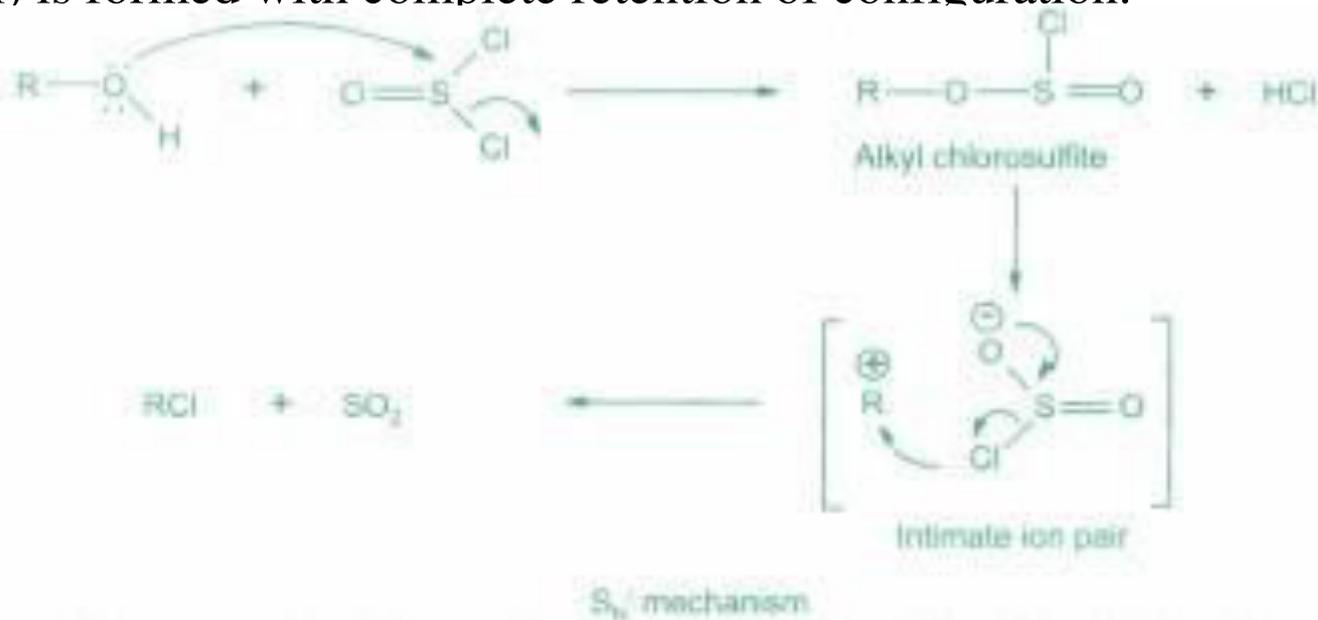


Allyl and benzyl halides not only react faster than simple halides in S_N1 reaction, but they react much faster than simple halides in S_N2 reaction as well. Allyl bromide, for example, is about 100 times more reactive towards simple S_N2 reactions than is propyl bromide. The double bond stabilizes the S_N2 transition state by conjugation with p orbital at the carbon atom under attack. Any stabilization of the transition state will, of course, accelerate the reaction by lowering the energy barrier.

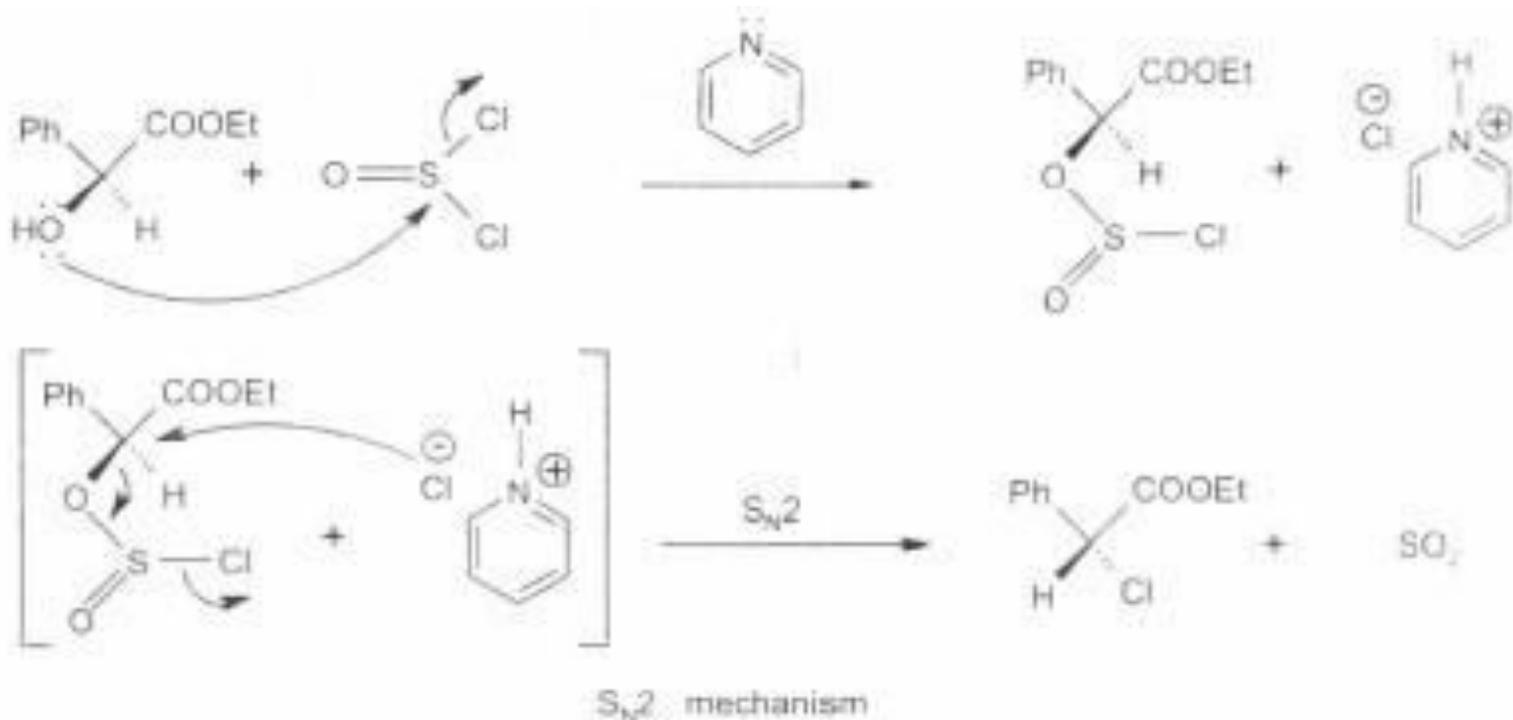


S_N^i (Substitution Nucleophilic internal)

In this process part of leaving group which attacks the substrate detaches itself from the rest of the leaving group. This is exemplified by the conversion of (R)-2-butanol to (R)-2-chlorobutane with SOCl_2 in nonpolar solvent and absence of base. The product formed is with complete retention of configuration, i.e., in which the starting material and product have the same configuration. The mechanism appears to involve the formation of intermediate chlorosulfite ester, ROSOCl (R = sec-butyl group), which dissociates into an intimate ion pair, $\text{R}^+ \cdot \text{-OSOCl}$ as in S_N1 mechanism. The Cl, with pair of electrons, of the anion attacks the R^+ from the same side of the carbocation from which -OSOCl departed and the product (RCl) is formed with complete retention of configuration.



It is interesting to note that if a tertiary amine such as pyridine is added to the reaction mixture, the product RCl is found now to have undergone inversion of configuration. The pyridine co-ordinates with the HCl, produced during the formation of intermediate chlorosulfite from ROH and SOCl₂, to form pyridine hydrochloride and the Cl⁻ is an effective nucleophile. The displacement of the chlorosulfite ester by Cl⁻ *via* S_N2 mechanism gives product with complete inversion of configuration. The reaction of alcohols with thionyl chloride in presence of pyridine is known as **Darzen's procedure**.



REFERENCE

□ V.K Ahluwalia

THANK YOU

Department of Chemistry

**Govt Dr Shyama Prasad Mukharjee Science and Commerce
College [Old Benazeer College]**

Topic:-Reaction intermediates

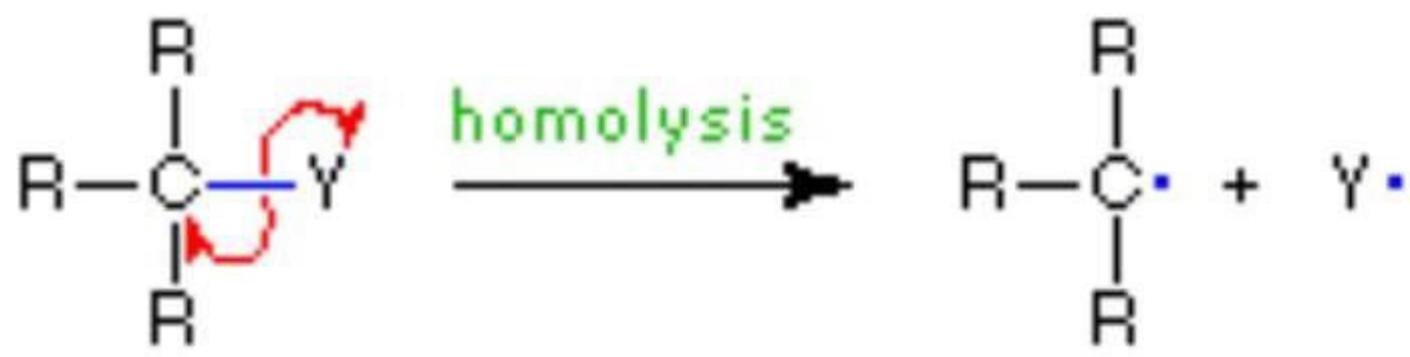
Presented By

Dr.Sudhanshu dhar

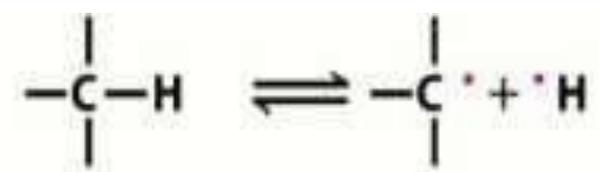
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Reaction Intermediates

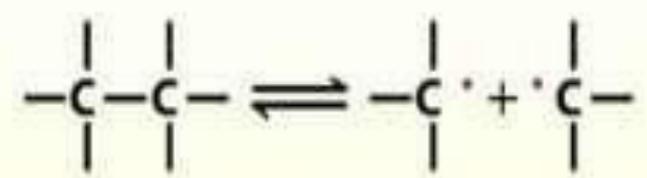
- In an organic reaction the molecule undergoing change are called reactants and the new molecules formed are called products. e.g.
- $$\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$$
- In this reaction a C-H bond and a Cl-Cl bond in the reactants have broken, and a new C-Cl bond and a H-Cl bond have formed in the product. There are two possible ways by which a covalent bond can break.
- **Homolytic Cleavage**:-The covalent bond between two elements can break in such a way that each element retains an electron of the bonding pair. The resulting fragments are called free radicals.



Homolytic cleavage

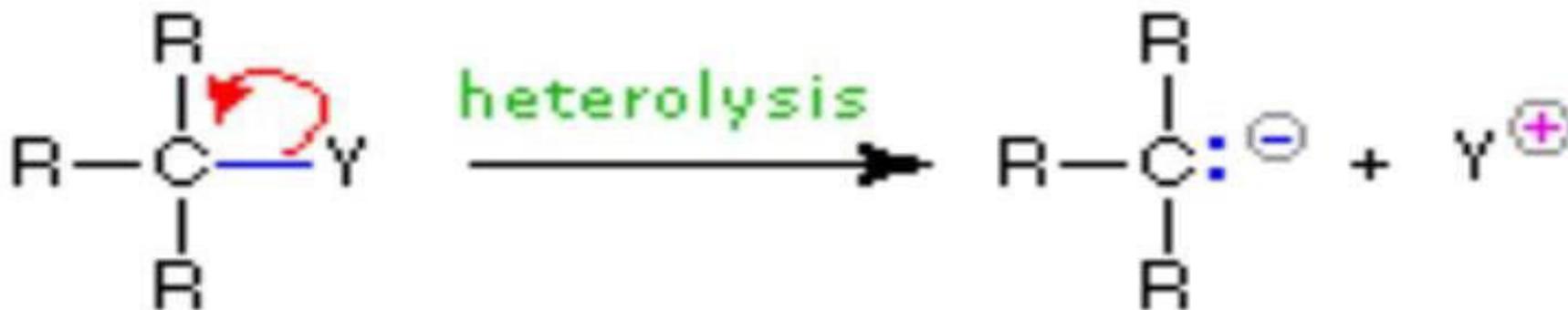
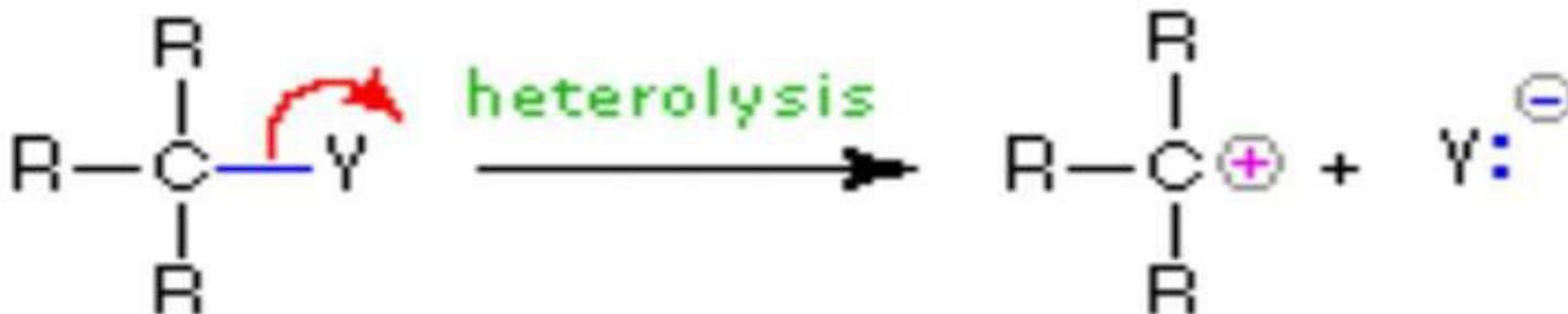


Carbon H atom radical

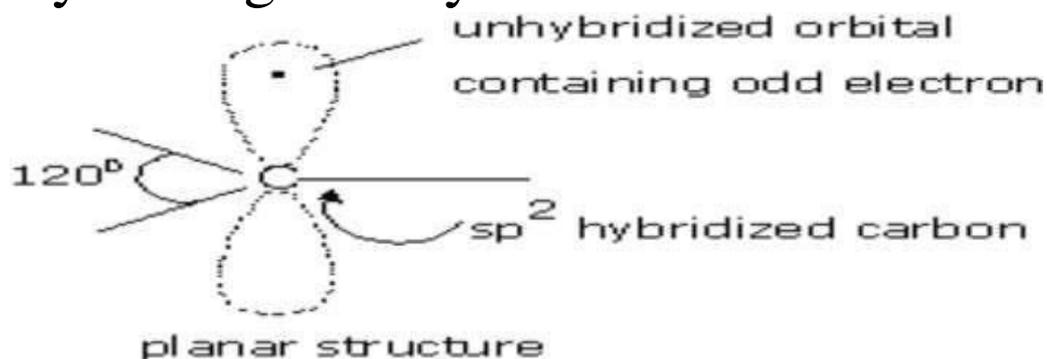


Carbon radicals

- **Heterolytic Cleavage:**-The bond between two atoms can break in another way in which one element retains the bonding pair and other loses, thus positively and negatively charged ions are formed. Reactions involving heterolytic cleavage are called ionic reactions.



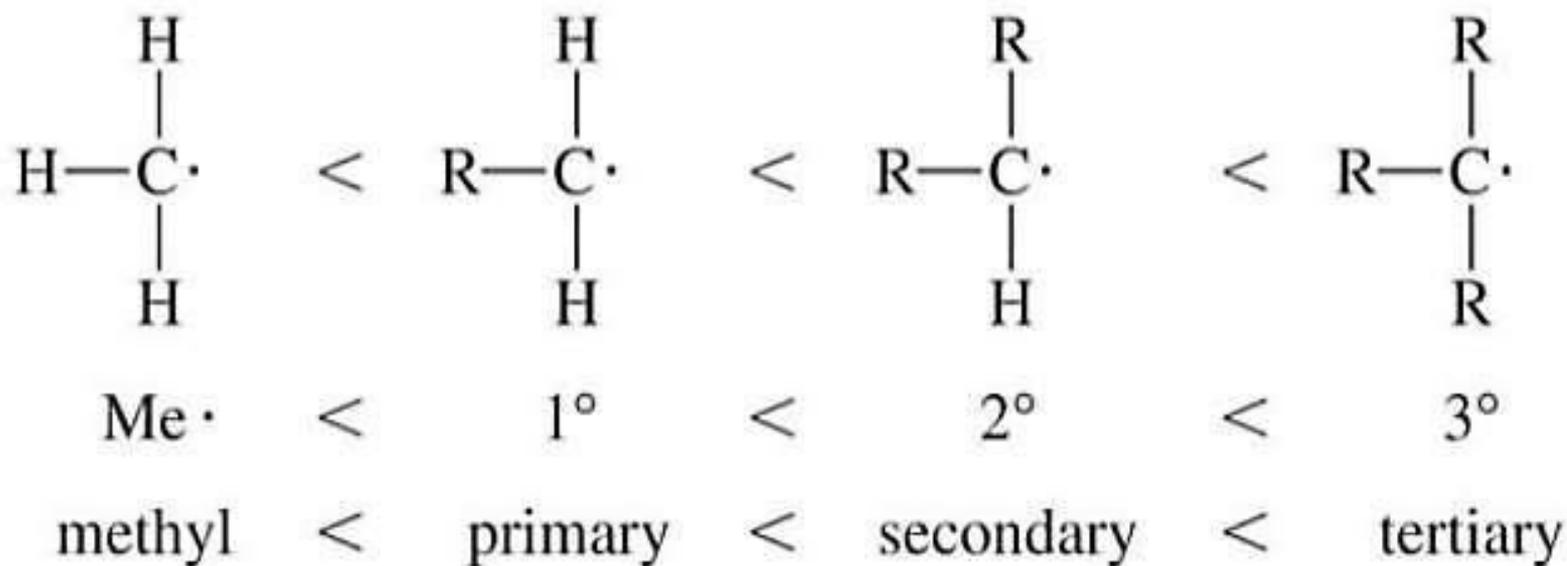
- These radicals and ions are called **intermediates**. So these intermediates are short lived (10^{-6} to few seconds) and highly reactive fragments formed from reactants or preceding intermediates and reacts further to give the directly observed products of a chemical reaction.
- **Carbon Radicals**:-Those in which the carbon carries one unpaired electron. usually formed by homolytic cleavage at high temp, by UV light or by addition of other radicals .e.g.



- Carbon radicals are neutral but are extremely reactive.
- It is supposed to be sp^2 or sp^3 hybridized.
- They are paramagnetic in character.

- **Stability of carbon radicals:**-Increases with the increase in the no of alkyl groups attached to carbon carrying odd electron by hyperconjugation.

Stability of Free Radicals

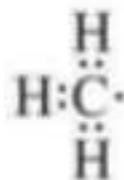
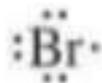


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- Free radicals are more stable if they are highly substituted.

Lewis Structures of Free Radicals

Lewis structures



Written



chlorine atom

bromine atom

hydroxyl radical

methyl radical

ethyl radical

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- Free radicals are unpaired electrons.
- Halogens have 7 valence electrons so one of them will be unpaired (radical). We refer to the halides as atoms not radicals.

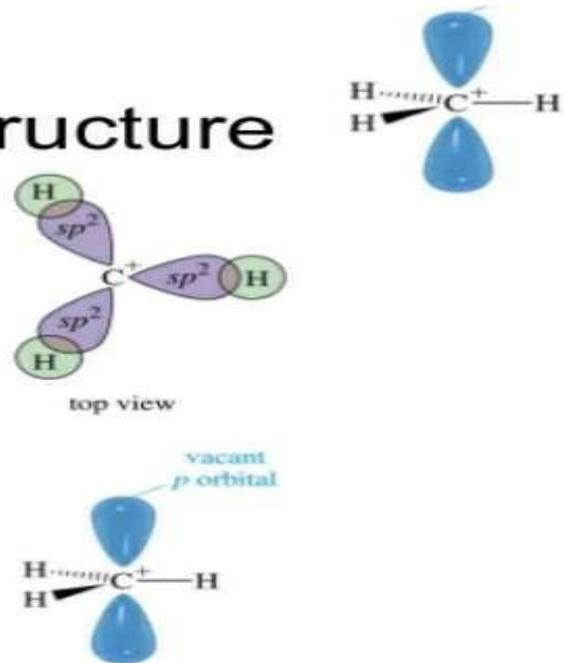
Carbocations

- Generally formed in acid catalyzed reactions .
- An ion in which the carbon carries a positive charge is called carbocation .There are formed by heterolysis .Carbon bearing a positive charge being sp^2 hybridized .
- **Geometrical shape:-**The carbocation takes up the more stable sp^2 configuration with the vacant $2p$ orbital at right angles to the plane of the sp^2 orbital's .

Carbocation Structure

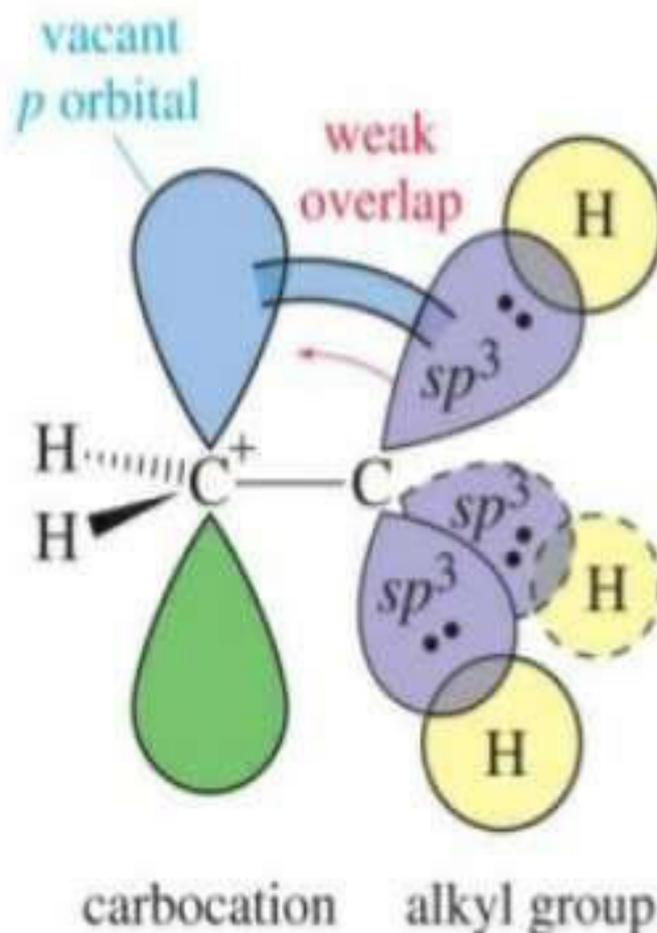
- Carbon has 6 electrons, positive charge.
- Carbon is sp^2 hybridized with vacant p orbital.

=>

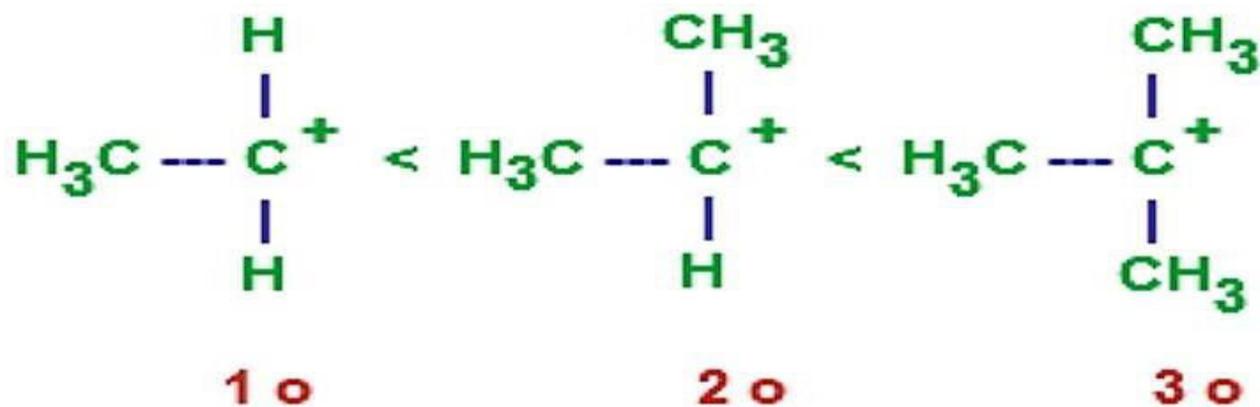


Carbocation Stability (Continued)

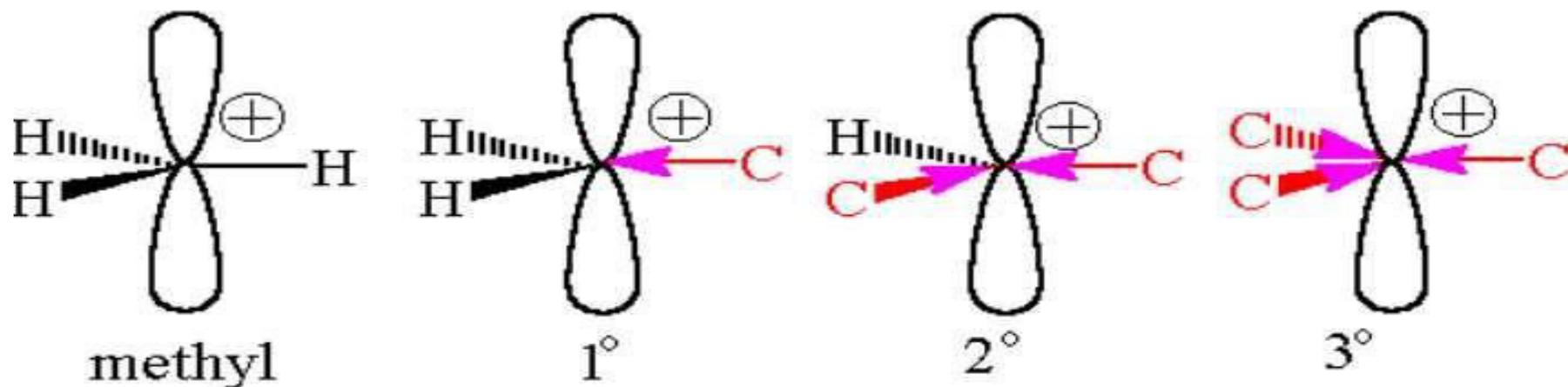
- Stabilized by alkyl substituents in two ways:
 - Inductive effect:** Donation of electron density along the sigma bonds.
 - Hyperconjugation:** Overlap of sigma bonding orbitals with empty p orbital.



- More stable a carbocation, more easily it is formed.

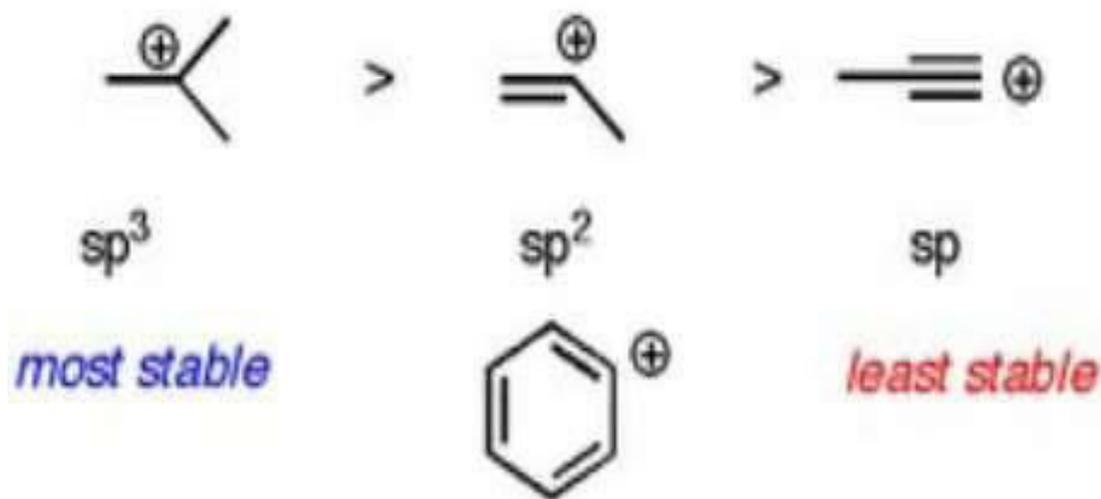


Inductive Stabilization of Carbocations

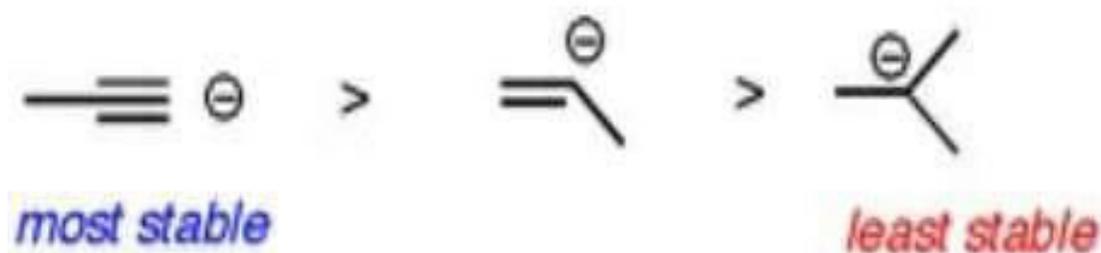


The more Carbons adjacent to the cation site, the more stable the cation. (Remember, Carbon releases electron density better than Hydrogen.)

Carbocations are **destabilized** as hybridization goes from $sp^3 \Rightarrow sp^2 \Rightarrow sp$

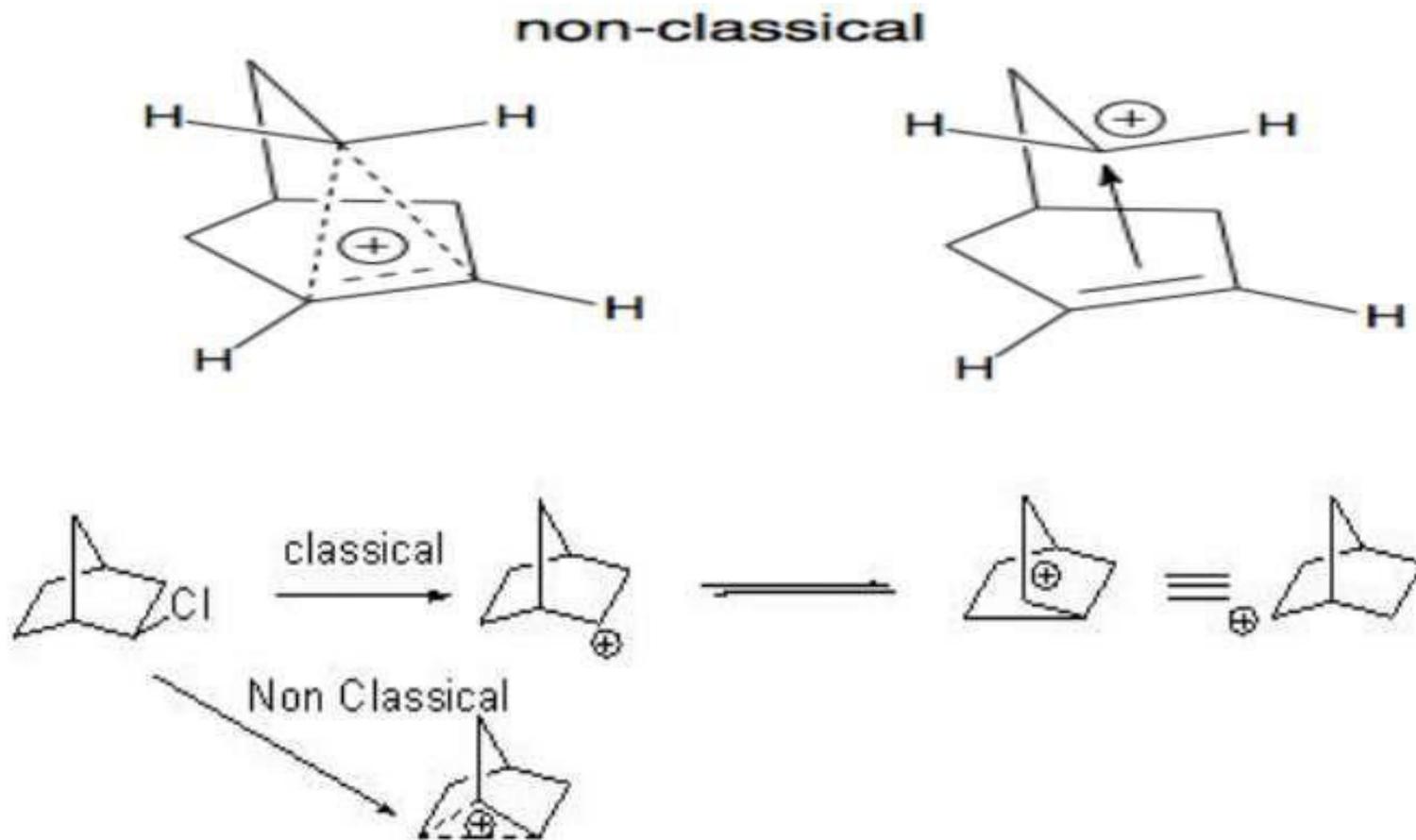


Think of this as the **opposite** of the effect of hybridization on carbanions



Non-Classical Carbocations

- Carbocations which are stabilized through participation of pi-bonds which are not in conjugation or those of σ -bonds are called non-classical carbocations. e.g.

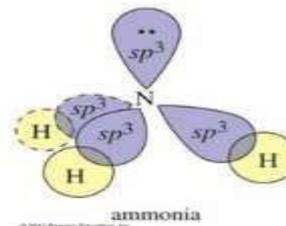
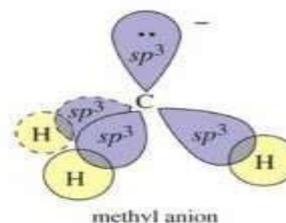


Carbanion

- Negatively charged organic species in which negative charge resides on the carbon atom. They are formed by heterolysis when a group departs from a molecule without the bonding pair of electrons.
- Carbon bearing negative charge is sp^3 hybridized. Three hybridized orbitals form three covalent bonds with atoms /groups .4th sp^3 hybrid orbital as non bonding pair of electrons.
- Pyramidal shape similar to ammonia.

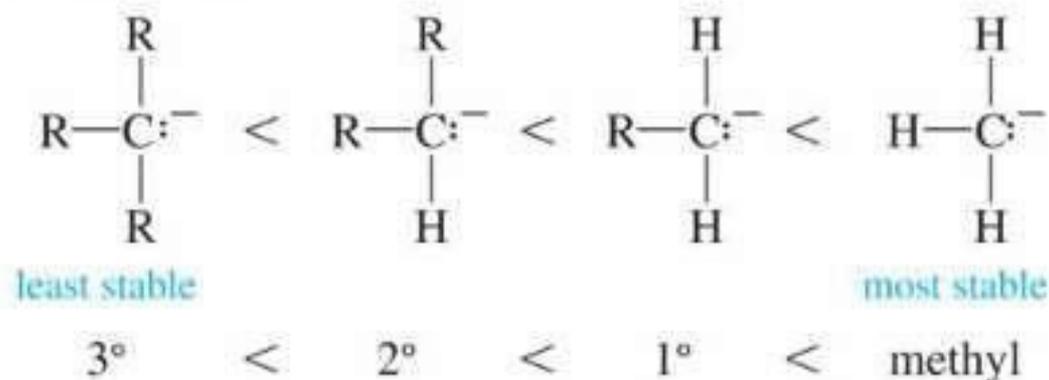
Carbanions

- Eight electrons on carbon: six bonding plus one lone pair.
- Carbon has a negative charge.
- Carbanions are nucleophilic and basic.



Stability of Carbanions

Stability of carbanions



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- Alkyl groups and other electron-donating groups slightly destabilize a carbanion.
- The order of stability is usually the opposite of that for carbocations and free radicals.

+I

HYDROGEN

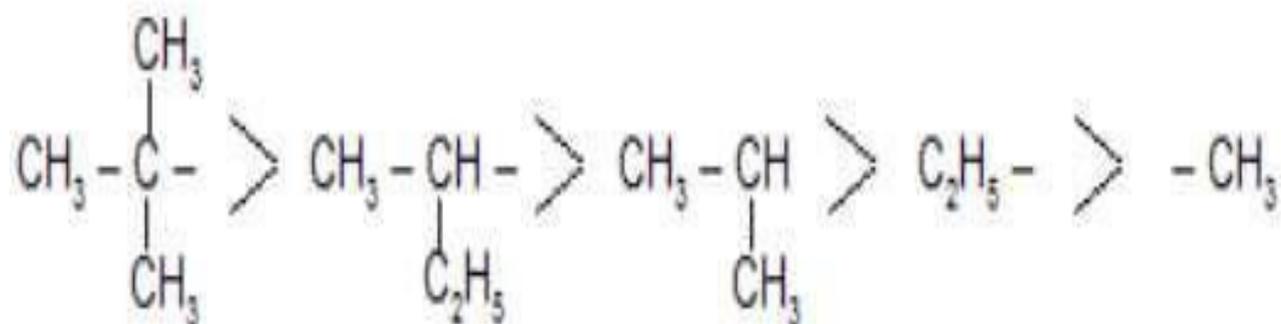
-I

Groups which attract electrons less strongly than hydrogen, electron donating groups, all alkyl groups.

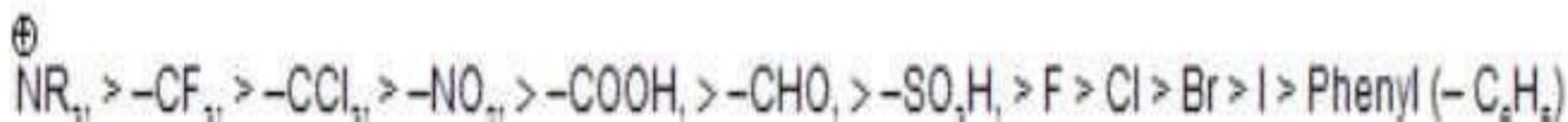
Strength of inductive effect (+I)

ZERO I effect

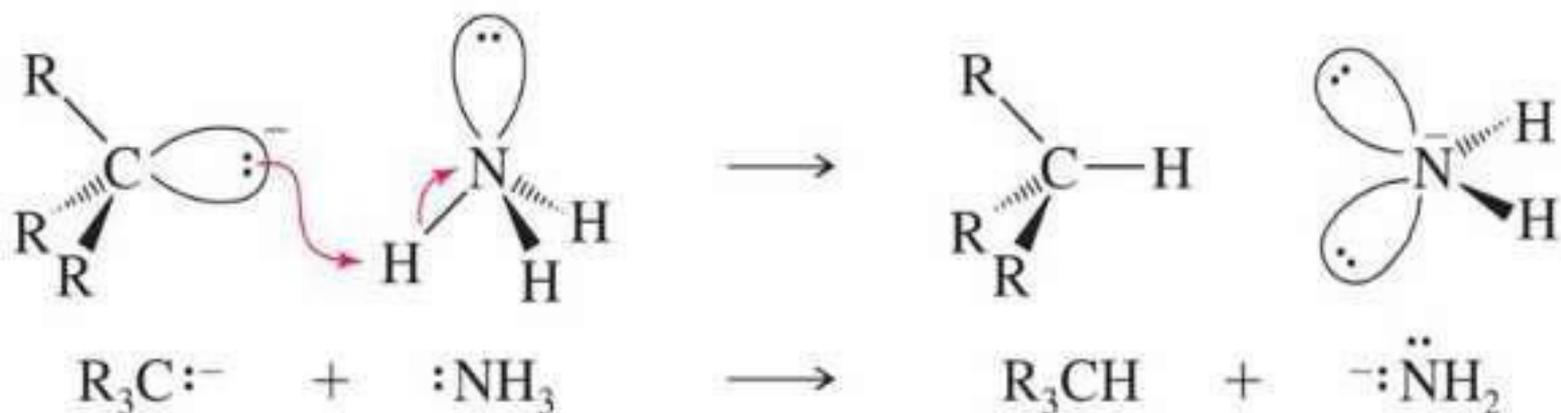
Groups which attract electrons more strongly than hydrogen electron attracting groups with high electronegativity
example $-\text{NO}_2$, $-\text{COOH}$



Strength of inductive effect (-I) in decreasing order



Basicity of Carbanions



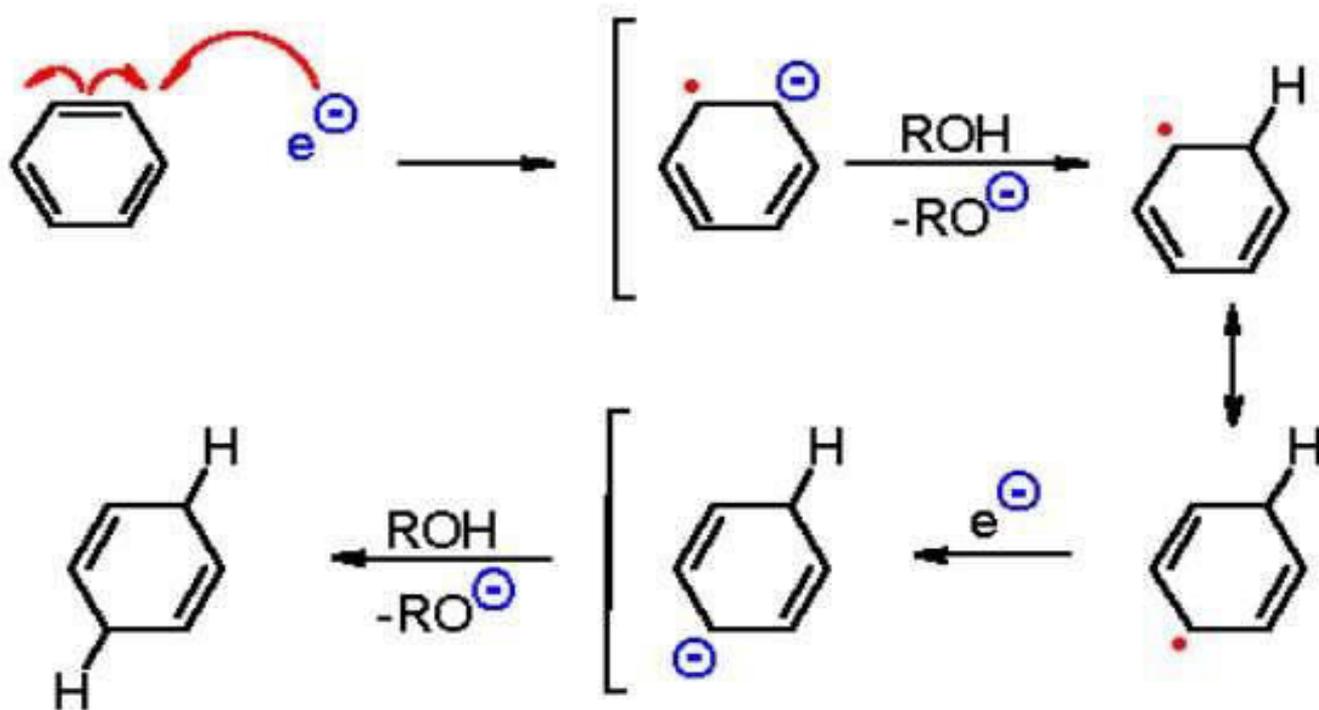
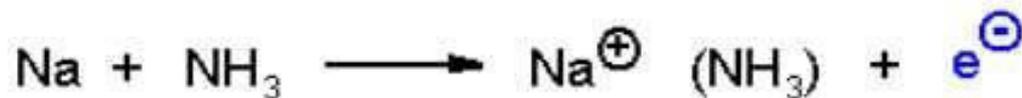
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- A carbanion has a negative charge on its carbon atom, making it a more powerful base and a stronger nucleophile than an amine.
- A carbanion is sufficiently basic to remove a proton from ammonia.

Radical Ions

- These are reaction intermediates in which both a radical and a charge is present.
- Generated during Birch reduction

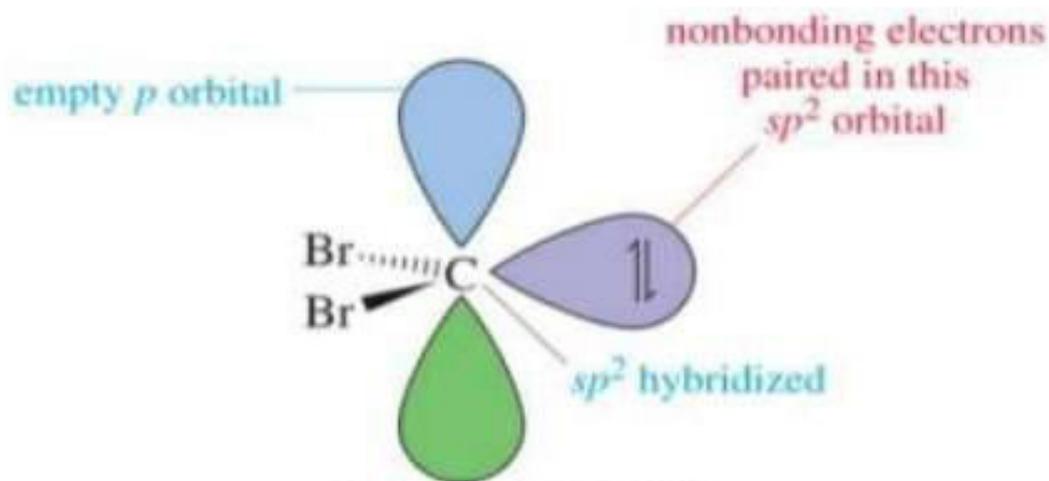
The Birch Reduction



Carbenes

- Carbenes are neutral species having a carbon atom with two bonds and two electrons.
- **Singlet Carbenes:** two electrons with opposite spins are paired in one orbital. Carbon atom is sp^2 hybridized.

Carbenes



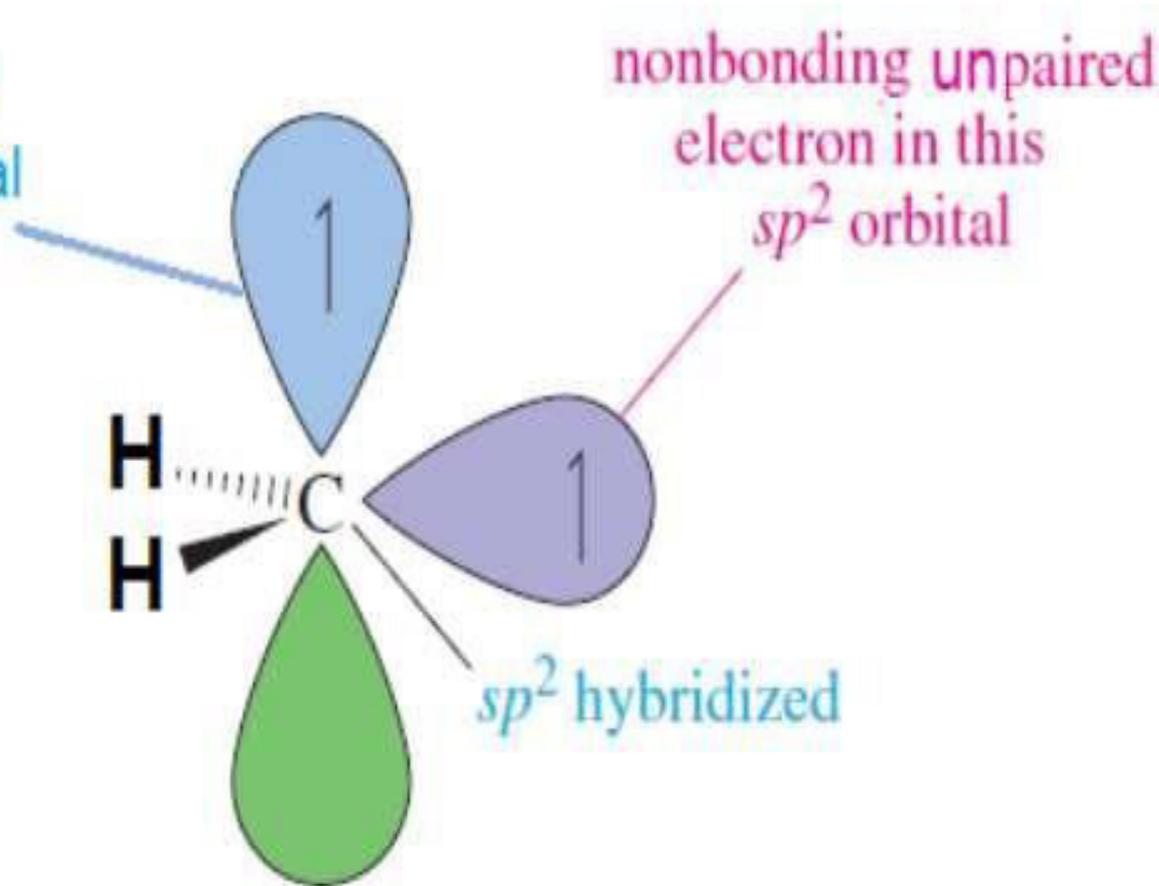
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- Carbon is neutral.
- Vacant p orbital, so can be electrophilic.
- Lone pair of electrons, so can be nucleophilic.

- **Triplet Carbenes:** electrons have same spin and in different orbital's. Sp hybridized. Triplet carbene is also called biradical.
- Triplet carbene is relatively more stable than singlet carbene due to inter-electronic repulsions in singlet state

Triplet Carbene

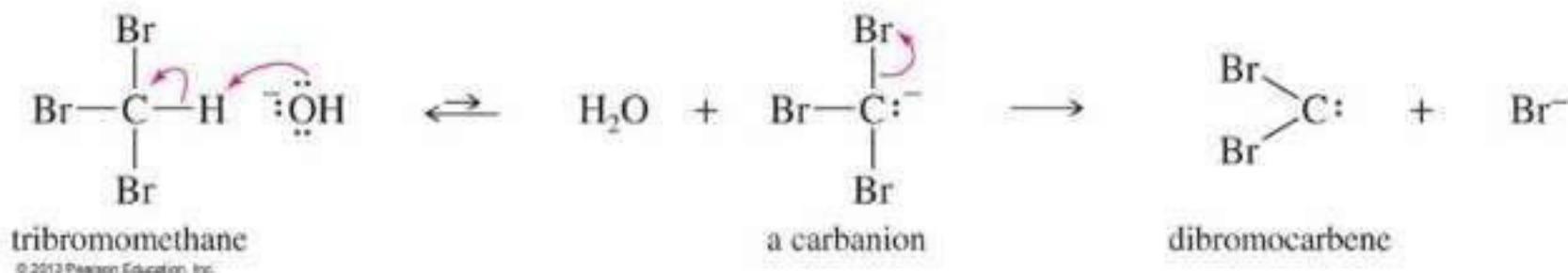
nonbonding unpaired electron in this p orbital



nonbonding unpaired electron in this sp^2 orbital

sp^2 hybridized

Carbenes as Reaction Intermediates



- A strong base can abstract a proton from tribromomethane (CHBr₃) to give an inductively stabilized carbanion.
- This carbanion expels bromide ion to give dibromocarbene. The carbon atom is sp^2 hybridized with trigonal geometry.
- A carbene has both a lone pair of electrons and an empty p orbital, so it can react as a nucleophile or as an electrophile.

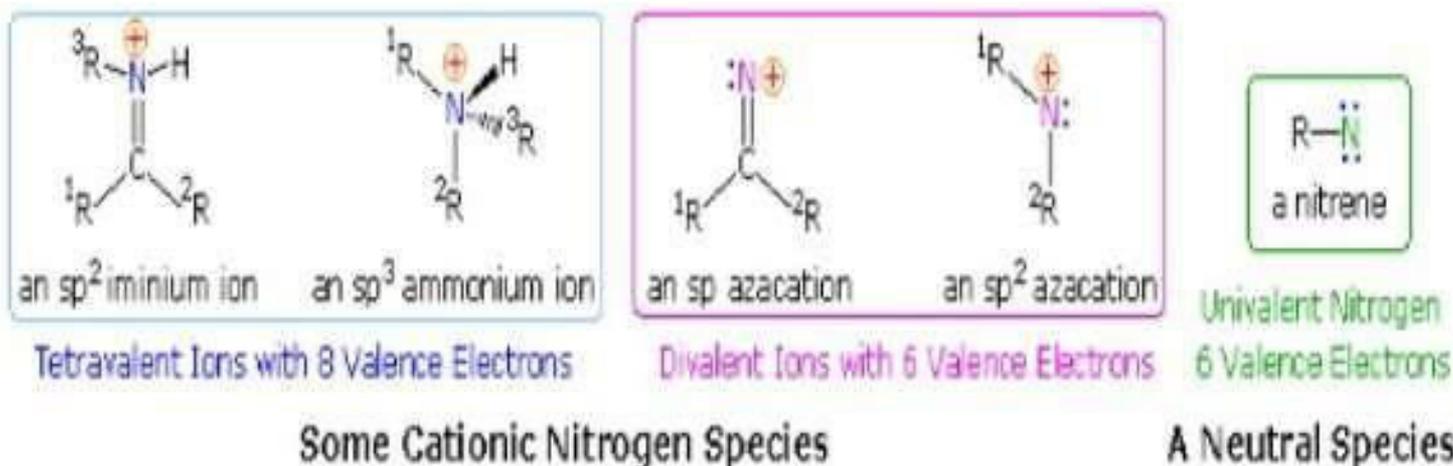
NITRENES

- These are neutral reaction intermediates where the central nitrogen atom is electron-deficient and has a sextet of electrons.



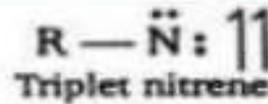
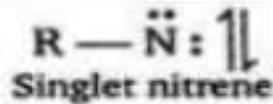
The structure of a typical nitrene group

- Sp^2 hybridized and planar in shape.

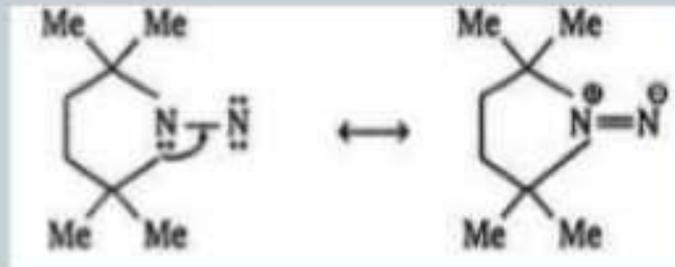


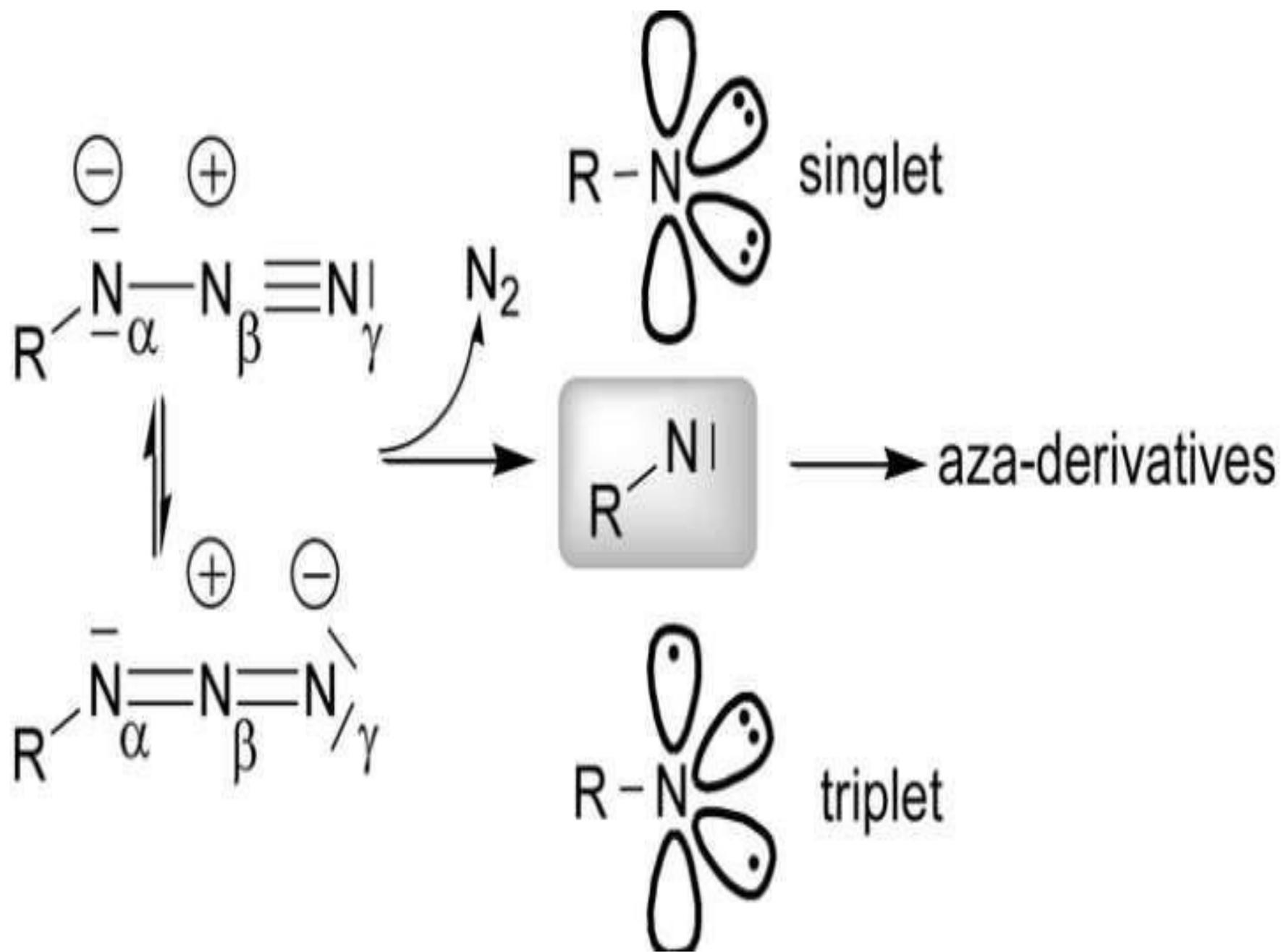
(2) NITRENES

1. Nitrenes are derivatives of the molecule :NH in which nitrogen is monovalent. The nitrogen atom in nitrenes has a sextet of electrons.
2. Similar to carbene, singlet and triplet states are possible for nitrenes.



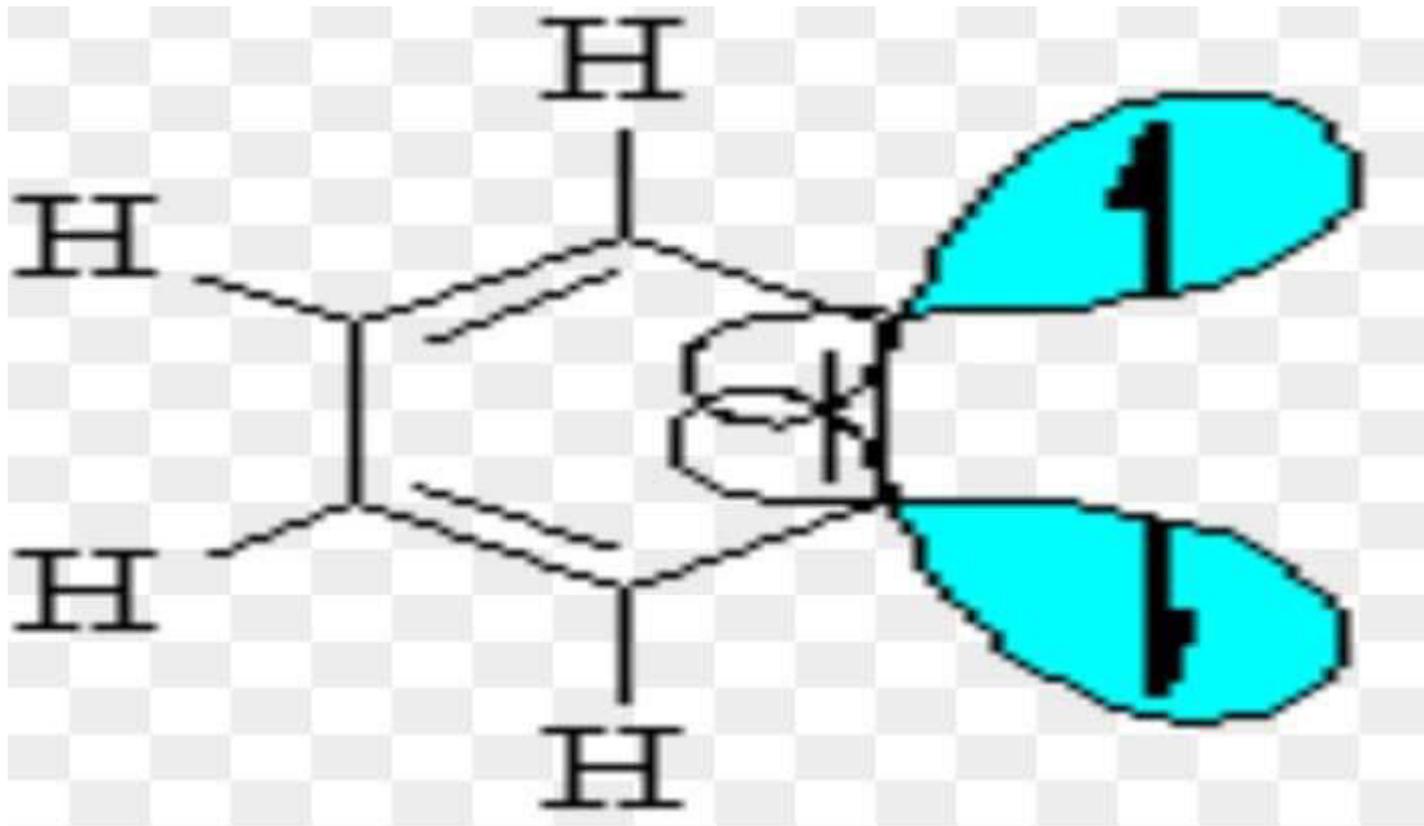
3. **Stability of Nitrenes:** As nitrogen is more electronegative it holds its electron closer to the nucleus which decreases energy and increases stability.

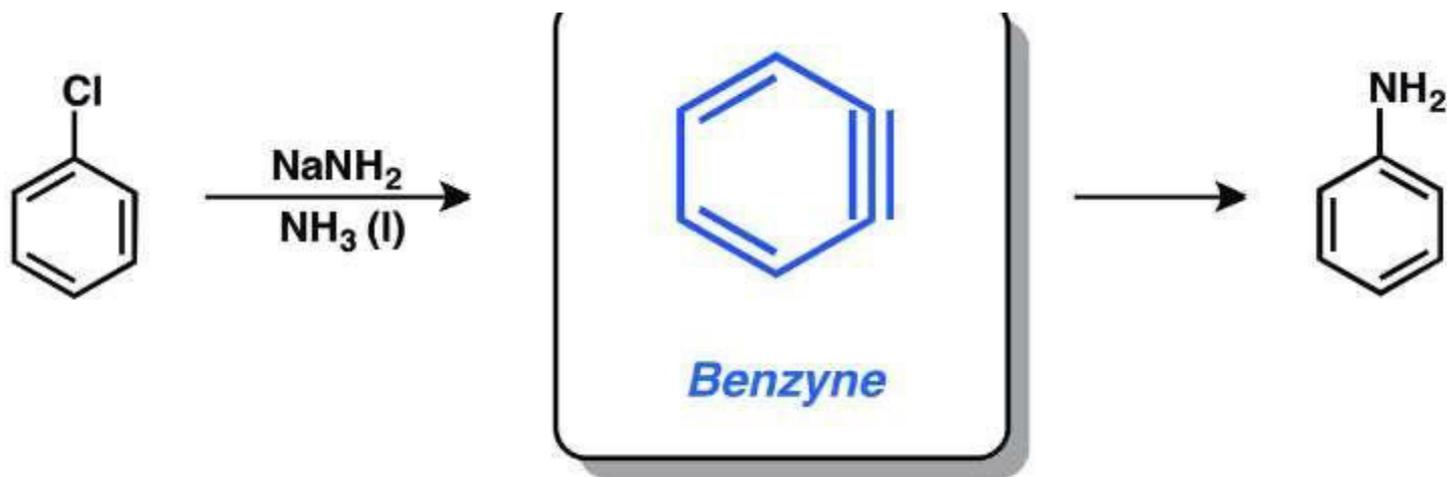
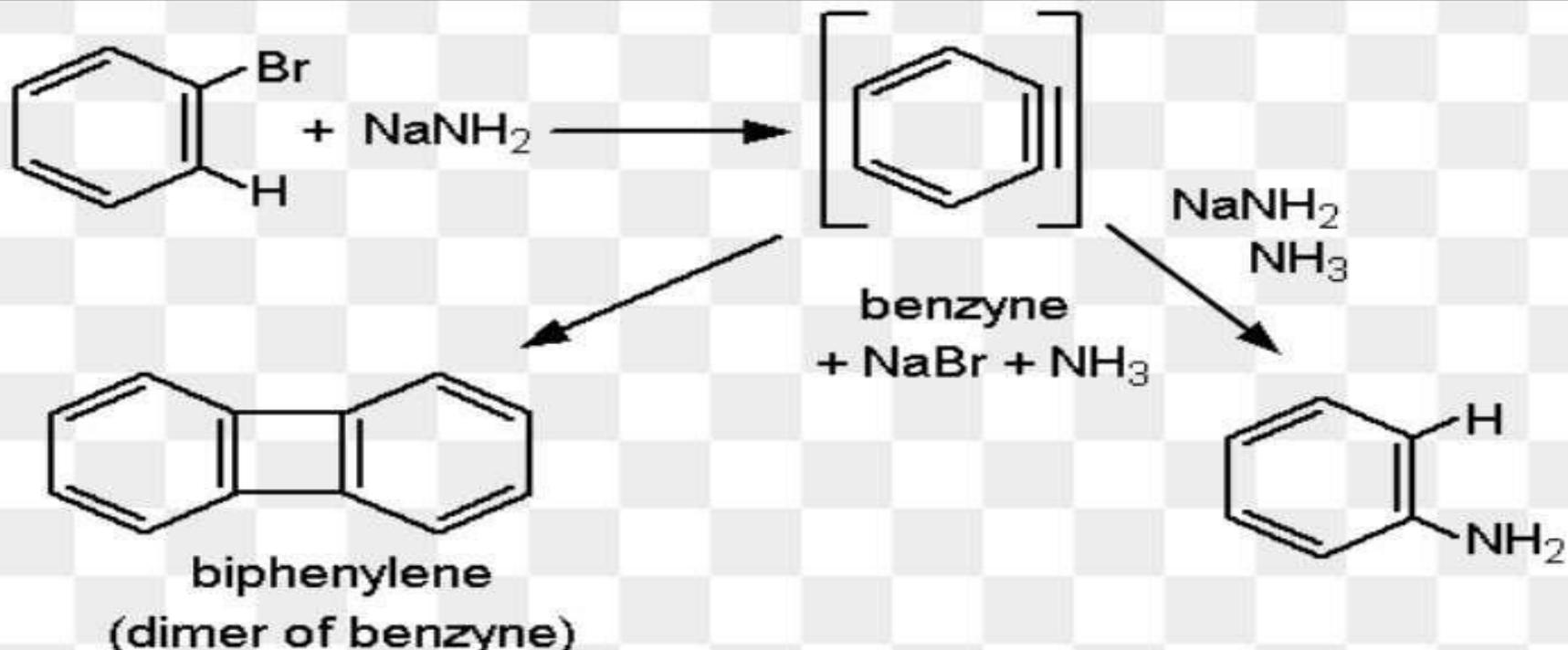


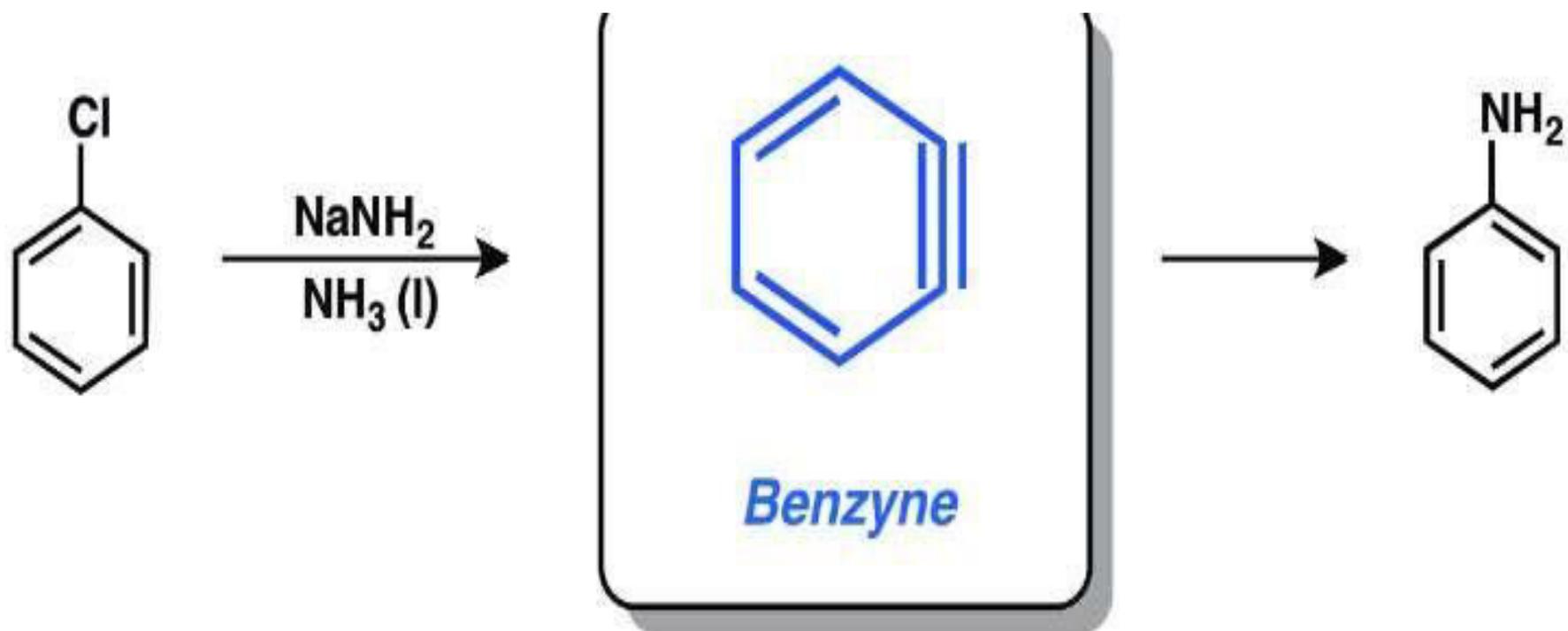
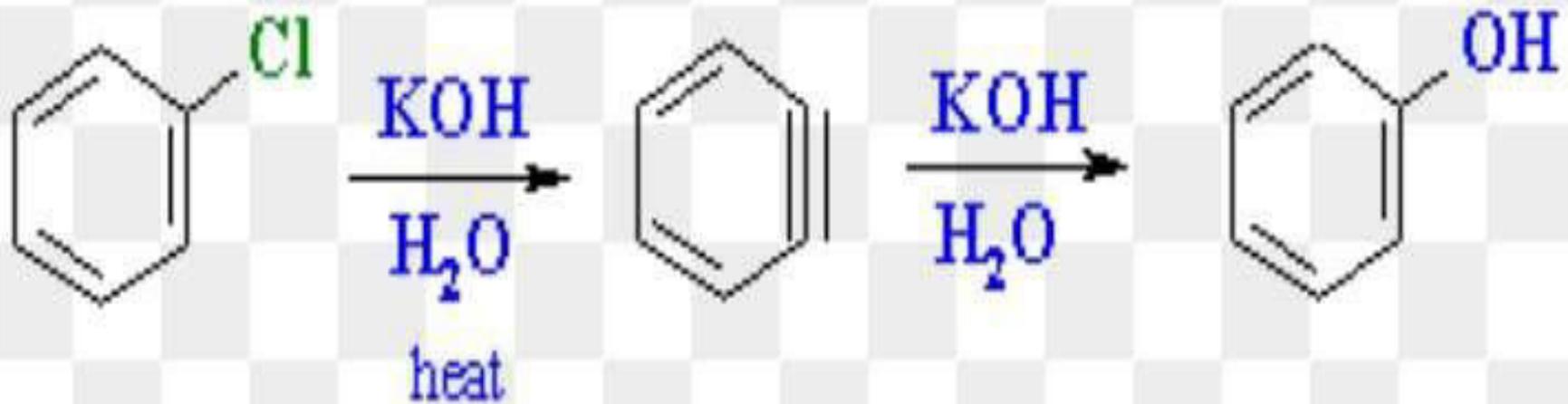


Benzynes

- Highly reactive intermediates generated during course of certain reactions.
- They have not been isolated.
- These are generated in certain aromatic compounds in the strong basic conditions.







Thanks To All of You

S_N1 & S_N2 Reaction

Professor Dr. S.D. Dwivedi

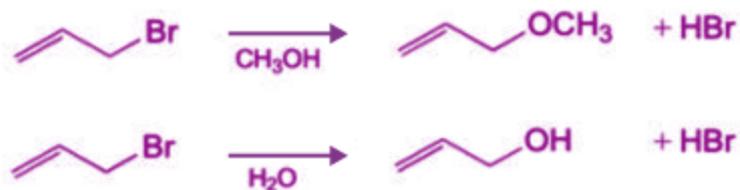
S_N1 REACTION

- S_N1 reaction mechanism follows a step-by-step process wherein first, the carbocation is formed from the removal of the leaving group. Then the carbocation is attacked by the nucleophile.
- Finally, the deprotonation of the protonated nucleophile takes place to give the required product. The rate-determining step of this reaction depends purely on the electrophilicity of the leaving group and is not impacted at all by the nucleophile.

What is an S_N1 Reaction?

- The S_N1 reaction is a nucleophilic substitution reaction where the rate-determining step is unimolecular. It is a type of organic substitution reaction. S_N1 stands for substitution nucleophilic unimolecular. Thus, the [rate equation](#) (which states that the S_N1 reaction is dependent on the electrophile but not on the nucleophile) holds in situations where the amount of the nucleophile is far greater than the amount of the carbocation intermediate.
- This reaction involves the formation of a carbocation intermediate. It is generally seen in the reactions of tertiary or secondary alkyl halides with secondary or tertiary alcohols under strongly acidic or strongly basic conditions. The S_N1 reaction is often referred to as the dissociative mechanism in inorganic chemistry. Given below are some examples of an S_N1 type of nucleophilic substitution reaction.

This reaction involves the formation of a carbocation intermediate. It is generally seen in the reactions of tertiary or secondary alkyl halides with secondary or tertiary alcohols under strongly acidic or strongly basic conditions. The S_N1 reaction is often referred to as the dissociative mechanism in inorganic chemistry. Given below are some examples of an S_N1 type of nucleophilic substitution reaction.

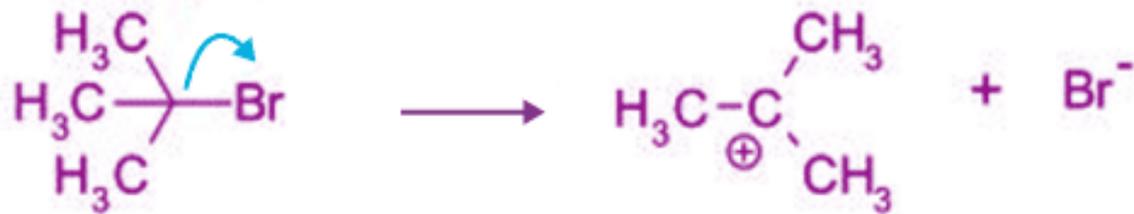


S_N1 Reaction Mechanism

Taking the hydrolysis of tertiary butyl bromide as an example, the mechanism of the S_N1 reaction can be understood via the following steps.

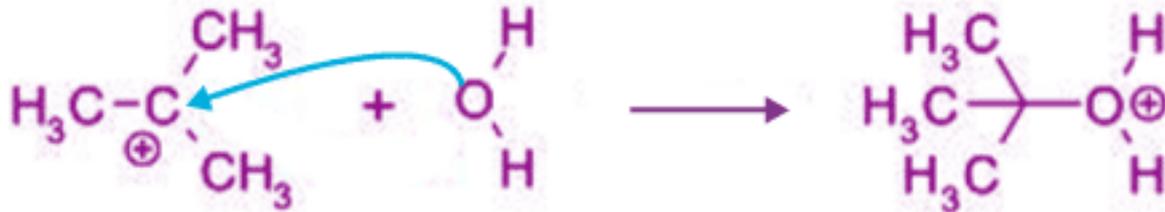
- **Step 1**
- The carbon-bromine bond is a polar covalent bond. The cleavage of this bond allows the removal of the leaving group (bromide ion).
- When the bromide ion leaves the tertiary butyl bromide, a carbocation intermediate is formed.
- As mentioned earlier, this is the rate-determining step of the S_N1 mechanism.
- It is important to note that the breaking of the carbon-bromine bond is endothermic.

STEP 1



Step-2

In the second step of the SN1 reaction mechanism, the carbocation is attacked by the nucleophile. Since water is used as a solvent, an oxonium ion intermediate is formed.



Step 3

The positive charge on the carbocation was shifted to the oxygen in the previous step.

The water solvent now acts as a base and deprotonates the oxonium ion to yield the required alcohol along with a hydronium ion as the product.

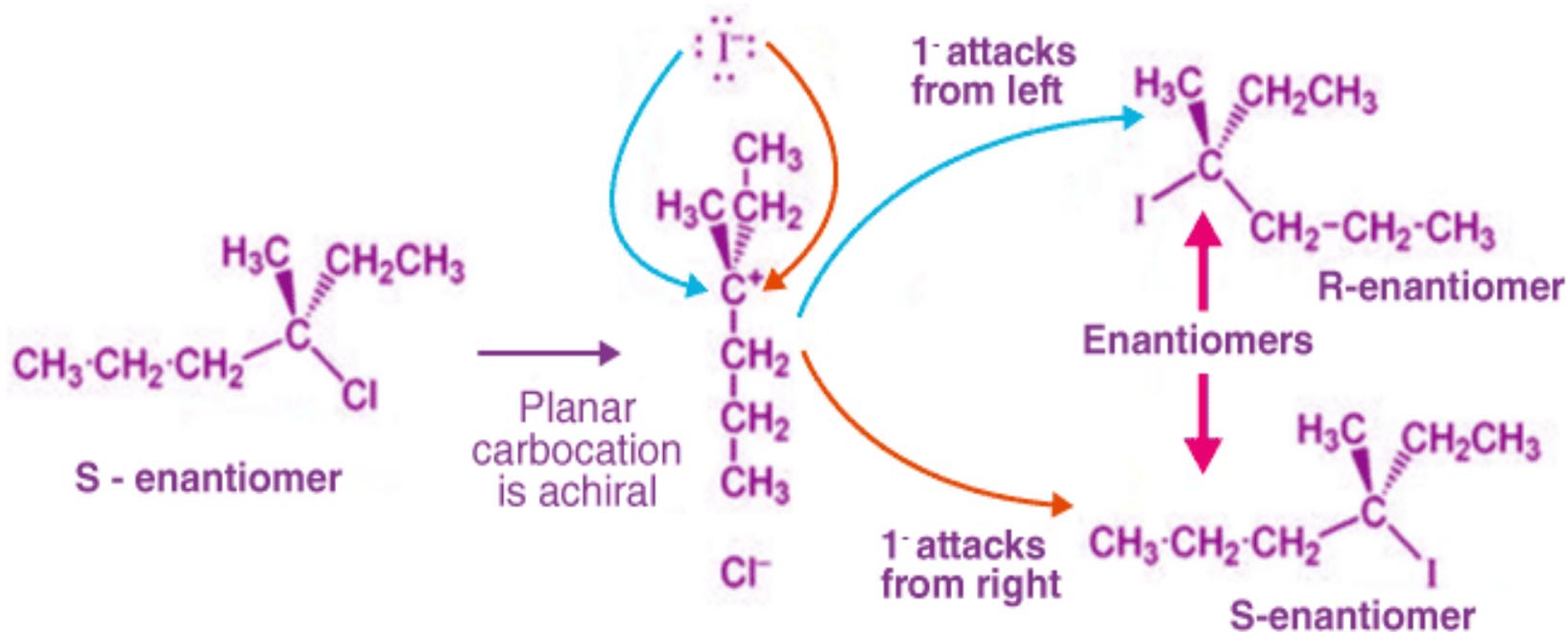
Step 2 and Step 3 of this reaction are fast.



Stereochemistry of S_N1 Reaction

- The carbocation intermediate formed in step 1 of the S_N1 reaction mechanism is an sp² hybridized carbon. Its molecular geometry is trigonal planar, therefore allowing for two different points of nucleophilic attack, left and right.
- If the reaction takes place at a stereocenter and if neither avenue for the nucleophilic attack is preferred, the carbocation is then attacked equally from both sides, yielding an equal ratio of left and right-handed enantiomers as shown below.

Stereochemistry of S_N1 Reaction



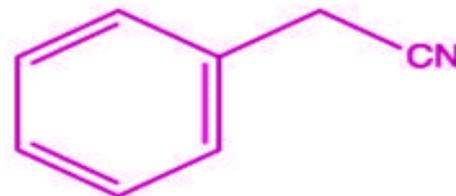
Effect of Solvent

- A solvent that can facilitate the formation of the carbocation intermediate will speed up the rate-determining step of the S_N1 reaction.
- The preferred solvents for this type of reaction are both polar and protic.
- The polar nature of the solvent helps to stabilize ionic intermediates whereas the protic nature of the solvent helps solvate the leaving group.
- Examples of solvents used in S_N1 reactions include water and alcohol. These solvents also act as nucleophiles.

S_N2 Reaction

- The S_N2 reaction is a nucleophilic substitution reaction where a bond is broken and another is formed synchronously. Two reacting species are involved in the rate determining step of the reaction. The *term 'S_N2' stands for – Substitution Nucleophilic Bimolecular*. This type of reaction is also referred to as bimolecular nucleophilic substitution, associative substitution, and interchange mechanism.

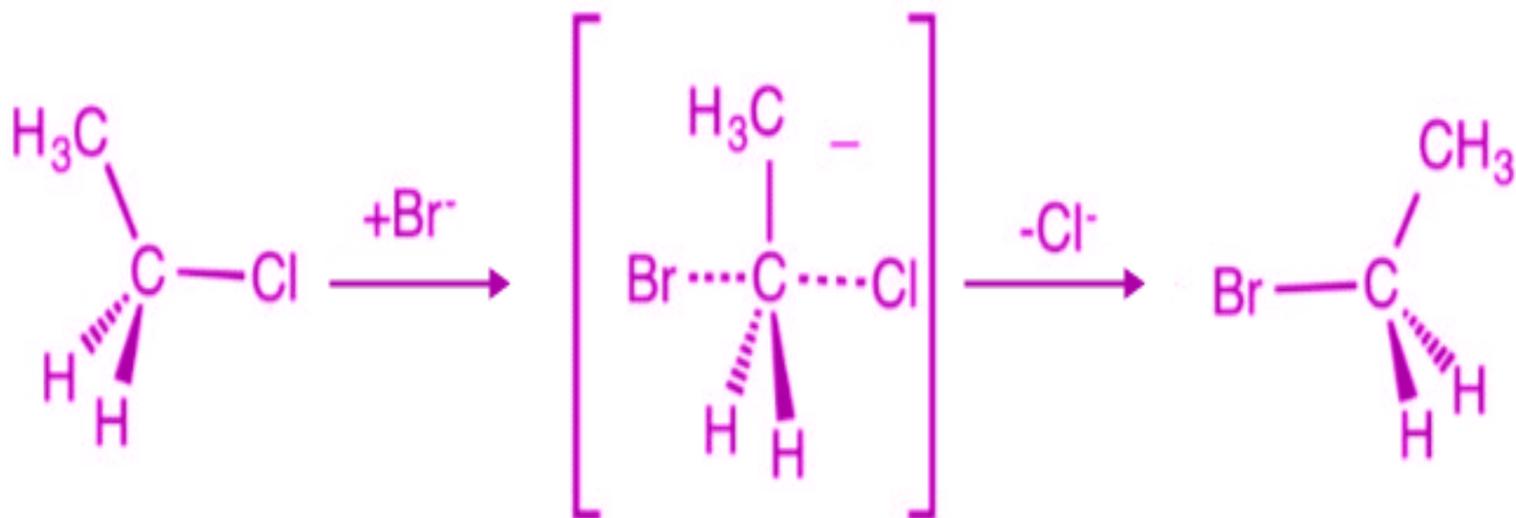
S_N2 Reaction



S_N2 Reaction Mechanism

- This reaction proceeds through a backside attack by the nucleophile on the substrate. The nucleophile approaches the given substrate at an angle of 180° to the carbon-leaving group bond. The carbon-nucleophile bond forms and carbon-leaving group ***bond breaks simultaneously through a transition state.***
- Now, the leaving group is pushed out of the transition state on the opposite side of the carbon-nucleophile bond, forming the required product. It is important to note that *the product is formed with an inversion of the tetrahedral geometry at the atom in the centre.*
- The S_N2 reaction mechanism for the nucleophilic substitution of chloroethane with bromine acting as the nucleophile is illustrated below.

S_N2 Reaction Mechanism



Stereochemistry of S_N2 Reactions

- There are two ways in which the nucleophile can attack the stereocenter of the substrate:
- A ***frontside attack*** where the nucleophile attacks from the same side where the leaving group is present, resulting in the retention of stereochemical configuration in the product.
- A ***backside attack*** where the nucleophile attacks the stereocenter from the opposite side of the carbon-leaving group bond, resulting in inversion of stereochemical configuration in the product.
- Since purely S_N2 reactions show ***100% inversion in stereochemical configuration***, it is clear that these Reactions occur through a ***backside attack***.

THANK YOU

CHROMATOGRAPHY

BSc I year

DR.SMITA VERMA
Govt.Dr. Shyama Prashad Mukherjee Science and
Commerce College Bhopal

History

Mikhail Tswett, Russian, 1872-1919

Botanist

In 1906 Tswett used to chromatography to separate plant pigments

He called the new technique chromatography because the result of the analysis was 'written in color' along the length of the adsorbent column

Chroma means “color” and graphein means to “write”

Chromatography is a physical method of separation in which the components to be separated are distributed between two phases

one of which is stationary (**stationary phase**) while the other (**the mobile phase**) moves through it in a definite direction.

The chromatographic process occurs due to differences in the **distribution constant** of the individual sample components

Chromatography

Is a technique used to separate and identify the components of a mixture

Works by allowing the molecules present in the mixture to distribute themselves between a stationary and a mobile medium.

Molecules that spend most of their time in the mobile phase are carried along faster.

Classification of chromatography according to mobile phase:

**1- Liquid chromatography: mobile phase is a liquid.
(LLC, LSC).**

**2- Gas chromatography : mobile phase is a gas.
(GSC, GLC).**

Classification according to the packing of the stationary phase:

1- Thin layer chromatography (TLC): the stationary phase is a thin layer supported on glass, plastic or aluminium plates.

2- Paper chromatography (PC): the stationary phase is a thin film of liquid supported on an inert support.

3- Column chromatography (CC): stationary phase is packed in a glass column.

Classification according to the force of separation:

- 1- Adsorption chromatography.**
- 2- Partition chromatography.**
- 3- Ion exchange chromatography.**
- 4- Gel filtration chromatography.**
- 5- Affinity chromatography.**

Thin layer chromatography (TLC)

is a method for identifying substances and testing the purity of compounds.

TLC is a useful technique because it is relatively quick and requires small quantities of material.

Separations in TLC involve distributing a mixture of two or more substances between a stationary phase and a mobile phase.

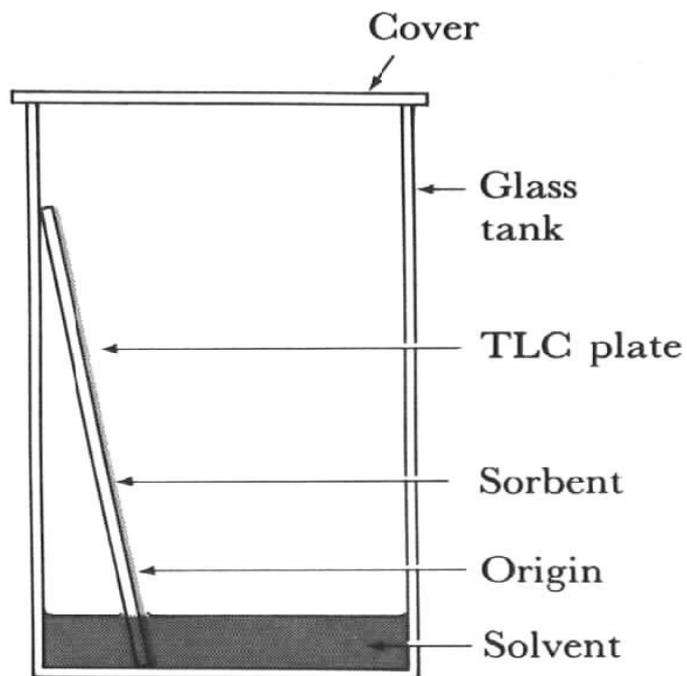
The stationary phase:

is a thin layer of adsorbent (usually silica gel or alumina) coated on a plate.

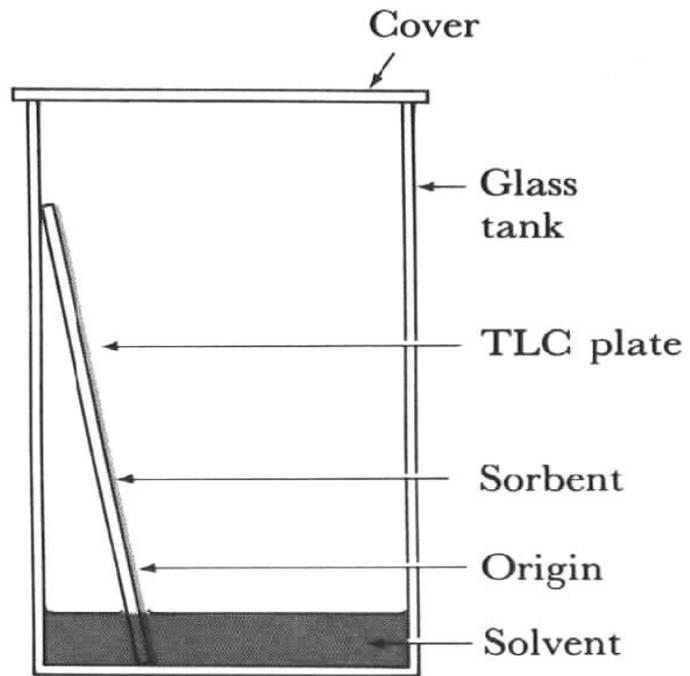
The mobile phase:

is a developing liquid which travels up the stationary phase, carrying the samples with it. Components of the samples will separate on the stationary phase according to how much they adsorb on the stationary phase versus how much they dissolve in the mobile phase.

Thin Layer Chromatography (TLC)



TLC



Preparing the Chamber

To a jar with a tight-fitting lid add enough of the appropriate developing liquid so that it is 0.5 to 1 cm deep in the bottom of the jar.

Close the jar tightly, and let it stand for about 30 minutes so that the atmosphere in the jar becomes saturated with solvent.

Preparing the Plates for Development

With a pencil, etch two small notches into the adsorbent about 2 cm from the bottom of the plate.

The notches should be on the edges of the plate, and each notch should be the same distance up from the bottom of the plate.

The notches must be farther from the bottom of the plate than the depth of the solvent in the jar.

Using a drawn-out capillary tube, spot the samples on the plate so that they line up with the notches you etched.

Developing the Plates

After preparing the development chamber and spotting the samples, the plates are ready for development.

Be careful to handle the plates only by their edges, and try to leave the development chamber uncovered for as little time as possible.

When the plates are removed from the chamber, quickly trace the solvent front (the highest solvent level on the plate) with a pencil.

Visualizing Agents

Alkaloids: Dragendorff's reagent

Cardiac glycosides: Antimony trichloride

Sugar: Aniline phthalate

Amino acids: Ninhydrin

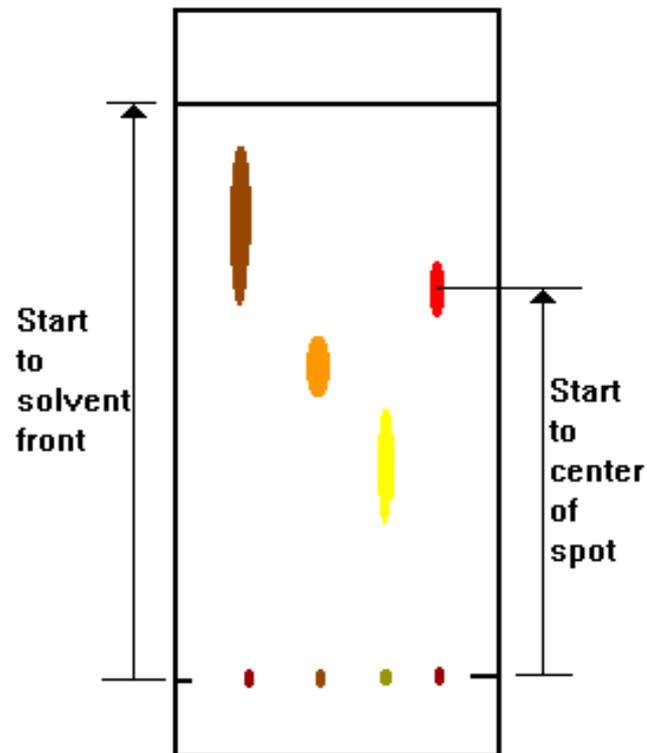
Interpreting the Data

The R_f (retention factor) value for each spot should be calculated.

It is characteristic for any given compound on the same stationary phase using the same mobile phase for development of the plates.

Hence, known R_f values can be compared to those of unknown substances to aid in their identifications.

$$R_f = \frac{\text{Distance from start to center of substance spot}}{\text{Distance from start to solvent front}}$$



Summary

A TLC plate is a sheet of glass, metal, or plastic which is coated with a thin layer of a solid adsorbent (usually silica or alumina).

A small amount of the mixture to be analyzed is spotted near the bottom of this plate.

The TLC plate is then placed in a shallow pool of a solvent in a developing chamber so that only the very bottom of the plate is in the liquid.

This liquid, or the eluent, is the mobile phase, and it slowly rises up the TLC plate by capillary action.

As the solvent moves past the spot that was applied, an equilibrium is established for each component of the mixture between the molecules of that component which are adsorbed on the solid and the molecules which are in solution.

International Year of Periodic Table

2019

Dr Ila Jain

Professor, Chemistry Department, Govt.S.P.M.Science and Commerce college,Bhopal

Periodic Table of the Elements

1 H Hydrogen 1.008																	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305											13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.065	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.972	35 Br Bromine 79.904	36 Kr Krypton 84.358
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [209]	85 At Astatine 209.987	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Nh Nihonium unknown	114 Fl Flerovium [289]	115 Mc Moscovium unknown	116 Lv Livermorium [293]	117 Ts Tennessine unknown	118 Og Oganesson unknown

57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.242	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

Alkali Metal	Alkaline Earth	Transition Metal	Basic Metal	Semimetal	Nonmetal	Halogen	Noble Gas	Lanthanide	Actinide
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Hydrogen	Sc - Scandium	Nb - Niobium	Pm - Promethium	Hg - Mercury	Md - Mendeleevium
He - Helium	Ti - Titanium	Mo - Molybdenum	Sm - Samarium	Tl - Thallium	No - Nobelium
Li - Lithium	V - Vanadium	Tc - Technetium	Eu - Europium	Pb - Lead	Lr - Lawrencium
Be - Beryllium	Cr - Chromium	Ru - Ruthenium	Gd - Gadolinium	Bi - Bismuth	Rf - Rutherfordium
B - Boron	Mn - Manganese	Rh - Rhodium	Tb - Terbium	Po - Polonium	Db - Dubnium
C - Carbon	Fe - Iron	Pd - Palladium	Dy - Dysprosium	At - Astatine	Sg - Seaborgium
N - Nitrogen	Co - Cobalt	Ag - Silver	Ho - Holmium	Rn - Radon	Bh - Bohrium
O - Oxygen	Ni - Nickel	Cd - Cadmium	Er - Erbium	Fr - Francium	Hs - Hassium
F - Fluorine	Cu - Copper	In - Indium	Tm - Thulium	Ra - Radium	Mt - Meitnerium
Ne - Neon	Zn - Zinc	Sn - Tin	Yb - Ytterbium	Ac - Actinium	Ds - Darmstadtium
Na - Sodium	Ga - Gallium	Sb - Antimony	Lu - Lutetium	Th - Thorium	Rg - Roentgenium
Mg - Magnesium	Ge - Germanium	Te - Tellurium	Hf - Hafnium	Pa - Protactinium	Cn - Copernicium
Al - Aluminum	As - Arsenic	I - Iodine	Ta - Tantalum	U - Uranium	Nh - Nihonium
Si - Silicon	Se - Selenium	Xe - Xenon	W - Tungsten	Np - Neptunium	Fl - Flerovium
P - Phosphorus	Br - Bromine	Cs - Cesium	Re - Rhenium	Pu - Plutonium	Mc - Moscovium
S - Sulfur	Kr - Krypton	Ba - Barium	Os - Osmium	Am - Americium	Lv - Livermorium
Cl - Chlorine	Rb - Rubidium	La - Lanthanum	Ir - Iridium	Cm - Curium	Ts - Tennessine
Ar - Argon	Sr - Strontium	Ce - Cerium	Pt - Platinum	Bk - Berkelium	Og - Oganesson
K - Potassium	Y - Yttrium	Pr - Praseodymium	Au - Gold	Cf - Californium	
Ca - Calcium	Zr - Zirconium	Nd - Neodymium	Hg - Mercury	Es - Einsteinium	
				Fm - Fermium	

https://youtu.be/rz4Dd1I_fX0

The Periodic Table of Chemical Elements is one of the most significant achievements in science, capturing the essence not only of chemistry, but also of physics and biology.

2019 will be the 150th anniversary since Dmitry Mendeleev discovered the Periodic System and has been proclaimed the “International Year of the Periodic Table of Chemical Elements” (IYPT2019).

Dmitri Ivanovich Mendeleev, a Russian chemist, was the most important contributor to the early development of the periodic table. Many periodic tables were made but the most important one was the Mendeleev periodic table.

In 1869, after the rejection of Newlands Octave Law, Mendeleev Periodic table came into the picture. In Mendeleev's periodic table, elements were arranged on the basis of the fundamental property, atomic mass, and chemical properties. During Mendeleev's work, only 63 elements were known. After studying the properties of every element, Mendeleev found that the properties of elements were related to atomic mass in a periodic way. He arranged the elements such that elements with similar properties fell into the same vertical columns of the periodic table.

Most elements on the periodic table are metals and have the *-ium* suffix. Halogen names usually end with *-ine*. Noble gas names usually have the *-on* ending.

Technetium was the first element to be made artificially. It is the lightest element that has only radioactive isotopes (none are stable).

Before a name and symbol are approved, an element may be referred to by its atomic number (e.g., element 120) or by its systematic element name. The systematic element name is a temporary name that is based on the atomic number as a root and the *-ium* ending as a suffix. For example, element 120 has the temporary name unbinilium.

The present periodic table has room for 118 elements. Elements aren't discovered or created in order of atomic number. Scientists are working on creating and verifying elements 119 and 120, which will change the appearance of the table, though they were working on element 120 before element 119. Most likely, element 119 will be positioned directly below francium and element 120 directly below radium. Chemists may create much heavier elements that may be more stable because of the special properties of certain combinations of proton and neutron numbers.

Symbol: Tc (Technetium) 43

Atomic Weight: 98.9072

Discovery: Carlo Perrier, Emilio Segre 1937 (Italy) found it in a sample of molybdenum that had been bombarded with neutrons; erroneously reported Noddack, Tacke, Berg 1924 as Masurium.

Electron Configuration: [Kr] 5s² 4d⁵

Word Origin: Greek technikos: an art or technetos: artificial; this was the first element made artificially.

Isotopes: Twenty-one isotopes of technetium are known, with atomic masses ranging from 90-111. Technetium is one of two elements with $Z < 83$ with no stable isotopes; all of technetium's isotopes are radioactive. (The other element is promethium.) Some isotopes are produced as uranium fission products.

Properties: Technetium is a silvery-gray metal that tarnishes slowly in moist air. Common oxidation states are +7, +5, and +4. The chemistry of technetium is similar to that of rhenium. Technetium is a corrosion inhibitor for steel and is an excellent superconductor at 11K and below.

Uses: Technetium-99 is used in many medical radioactive isotope tests. Mild carbon steels may be effectively protected by minute quantities of technetium, but this corrosion protection is limited to closed systems because of technetium's radioactivity.

Transition Elements and their Properties

Dr Neelam Dubey, Professor, Chemistry Department, Govt. M.V.M. Bhopal

The IUPAC definition defines a transition metal as "an element whose atom has a partially filled d sub-shell, or which can give rise to cations with an incomplete *d* sub-shell".

English chemist Charles Bury (1890–1968) first used the word *transition* in this context in 1921, when he referred to a *transition series of elements* during the change of an inner layer of electrons (for example $n = 3$ in the 4th row of the periodic table) from a stable group of 8 to one of 18, or from 18 to 32.^{[5][6][7]} These elements are now known as the d-block.

Transition metal compounds are paramagnetic when they have one or more unpaired *d* electrons.

The transition metals and their compounds are known for their homogeneous and heterogeneous catalytic activity.

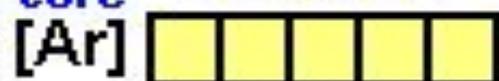
Transition-metal ions form **coordination** complexes because they have empty valence-shell orbitals that can accept pairs of electrons from a Lewis base.

Properties of transition elements include:

- have large charge/radius ratio;
- are hard and have high densities;
- have high melting and boiling points;
- form **compounds** which are often paramagnetic;
- show variable oxidation states;
- form coloured ions and **compounds**;
- form **compounds** with profound catalytic activity;

argon
core

3d orbitals



eg Sc³⁺ colourless NOT trans.



eg Ti³⁺ violet, V²⁺ violet



eg V³⁺ blue-green



eg Cr³⁺ violet-green



eg Cr²⁺ blue, Mn³⁺ violet



eg Mn²⁺ pale pink, Fe³⁺ yellow
-brown



eg Fe²⁺ green, Co³⁺ coloured
-unstable



eg Co²⁺ pink-blue



eg Ni²⁺ green



eg Cu²⁺ blue

(c) doc b



eg Cu⁺ colourless, Zn²⁺ NOT trans.

Elements of second transition series		Elements of third transition series	
Y	$[\text{Kr}]4d^15s^2$	La	$[\text{Xe}]5d^16s^2$
Zr	$[\text{Kr}]4d^25s^2$	Hf	$[\text{Xe}]4f^{14}5d^26s^2$
Nb	$[\text{Kr}]4d^45s^1$	Ta	$[\text{Xe}]4f^{14}5d^36s^2$
Mo	$[\text{Kr}]4d^55s^1$	W	$[\text{Xe}]4f^{14}5d^46s^2$
Tc	$[\text{Kr}]4d^65s^1$	Re	$[\text{Xe}]4f^{14}5d^56s^2$
Ru	$[\text{Kr}]4d^75s^1$	Os	$[\text{Xe}]4f^{14}5d^66s^2$
Rh	$[\text{Kr}]4d^85s^1$	Ir	$[\text{Xe}]4f^{14}5d^76s^2$
Pd	$[\text{Kr}]4d^{10}5s^0$	Pt	$[\text{Xe}]4f^{14}5d^96s^1$
Ag	$[\text{Kr}]4d^{10}5s^1$	Au	$[\text{Xe}]4f^{14}5d^{10}6s^1$
Cd	$[\text{Kr}]4d^{10}5s^2$	Hg	$[\text{Xe}]4f^{14}5d^{10}6s^2$

Transition [elements](#) form coloured [compounds](#) because they have unfilled d orbitals.

Here are the colours of some transition metal ions in aqueous solution.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3	+3	
	+4	+4	+4	+4	+4	+4	+4		
	+5	+5	+5	+5	+5	+5			
			+6	+6	+6				
				+7					

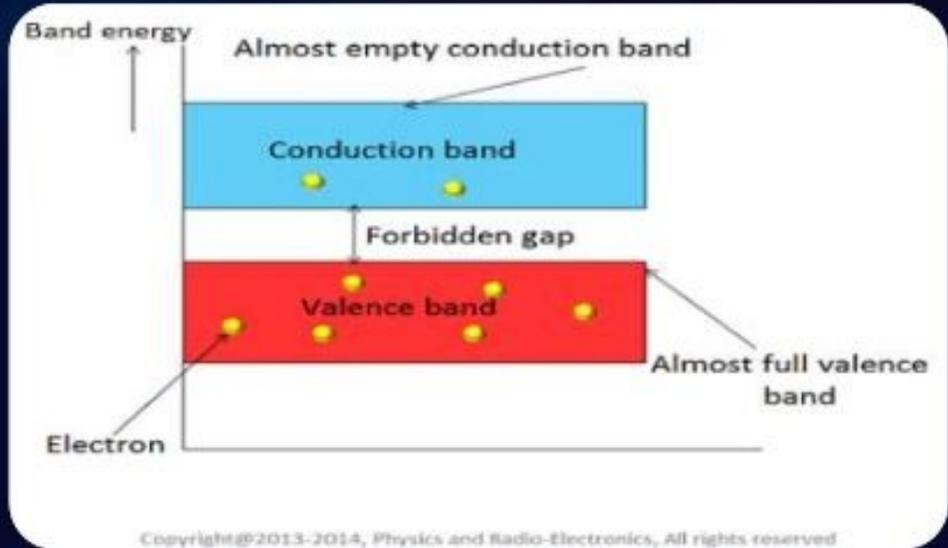
Metalloids and their Semiconductor Behavior

Dr. Bharti Jain

Professor. Chemistry Department, Govt. M.L.B. Girls P.G. College, Bhopal

Metalloids		Nonmetals		
Boron	Carbon	Nitrogen	Oxygen	Fluorine
5 <u>B</u>	6 <u>C</u>	7 <u>N</u>	8 O	9 F
Aluminum	Silicon	Phosphorus	Sulfur	Chlorine
13 <u>Al</u>	14 <u>Si</u>	15 <u>P</u>	16 <u>S</u>	17 Cl
Gallium	Germanium	Arsenic	Selenium	Bromine
31 <u>Ga</u>	32 <u>Ge</u>	33 As	34 <u>Se</u>	35 <u>Br</u>
Indium	Tin	Antimony	Tellurium	Iodine
49 <u>In</u>	50 <u>Sn</u>	51 <u>Sb</u>	52 Te	53 <u>I</u>
Thallium	Lead	Bismuth	Polonium	Astatine
81 Tl	82 <u>Pb</u>	83 <u>Bi</u>	84 Po	85 At
	Metals			

Semiconductors



S.No	Aspect	Conductors	Semiconductors	Insulators
1	Conductivity variation	Conductivity decreases with increase in temperature up to nearly zero value.	conductivity increases with increases in temperature. Conductivity is particularly sensitive to impurity type and consent.	Conductivities increases with increase in temperature.
2	Conductivity order	Conductivity of metals is of the order of 10^7 ($\Omega\text{-m}$) ⁻¹	Conductivity of semiconductors range from 10^{-6} to 10^4 ($\Omega\text{-m}$) ⁻¹ .	The conductivity of insulators ranges between 10^{-10} to 10^{-20} ($\Omega\text{-m}$) ⁻¹ .
3	Electrical resistivity	Electrical resistivity is very low and ranges from 10^{-9} to 10^{-4} ($\Omega\text{-m}$).	Resistivity is normally high and ranges between 10^{-3} to 10^3 ($\Omega\text{-m}$).	Resistivity is very high and ranges between 10^4 to 10^{17} ($\Omega\text{-m}$).
4	Temperature coefficient	Temperature coefficient of resistance is not constant.	The temperature coefficient of resistance is negative.	Negative resistance temperature coefficient. Probably with the rise in temperature some electrons reach to the



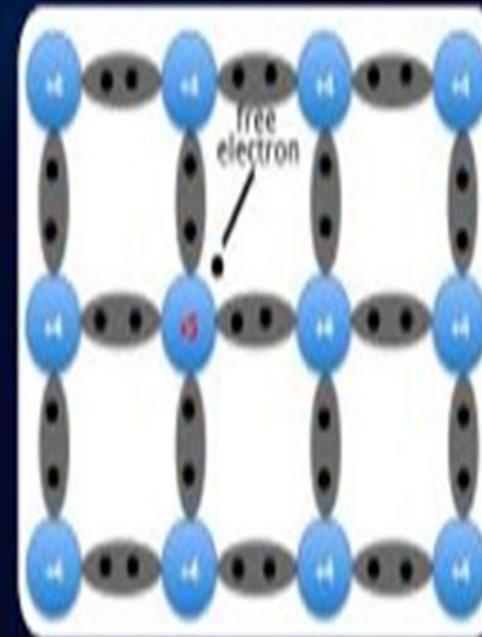
				conduction band.
5	Property with temperature variation	At low temperatures they exhibit semiconductivity. At very low temperatures, some elements and their alloys exhibit infinite conductivity, i.e. superconductivity.	At low temperature, semiconductors become dielectrics (insulators).	No change in properties of the insulated observed.
6	Energy bands	Have unfilled overlapping energy bands.	Have filled energy bands and small forbidden zones.	There is a large energy gap in between valence and conduction band.
7	Current carriers	Current carriers in conductors are free electrons which exist whether the external field is applied or not.	Current carriers are originated due to absorption of electrical, radiant or thermal energy from the external source. Electrons and holes, both serve as current carriers.	The energy required for electrons to cross the energy gap between conduction band and valence band is very large and hence no conduction.



❖ N-Type Semiconductors

- ❖ In addition to replacing one of the lattice atoms with a Group 3 atom, we can also replace it by an atom with five valence electrons, such as the Group 5 atoms arsenic (As) or phosphorus (P). In this case, the impurity adds five valence electrons to the lattice where it can only hold four. This means that there is now one excess electron in the lattice (see figure below). Because it donates an electron, a Group 5 impurity is called a donor. Note that the material remains electrically neutral.

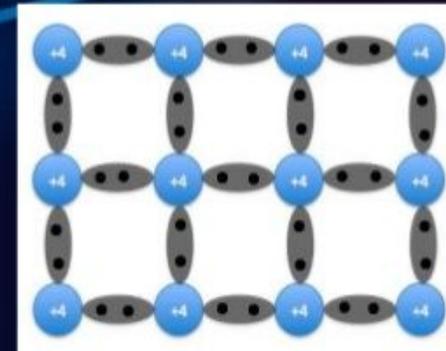
❖ N-Type Semiconductors



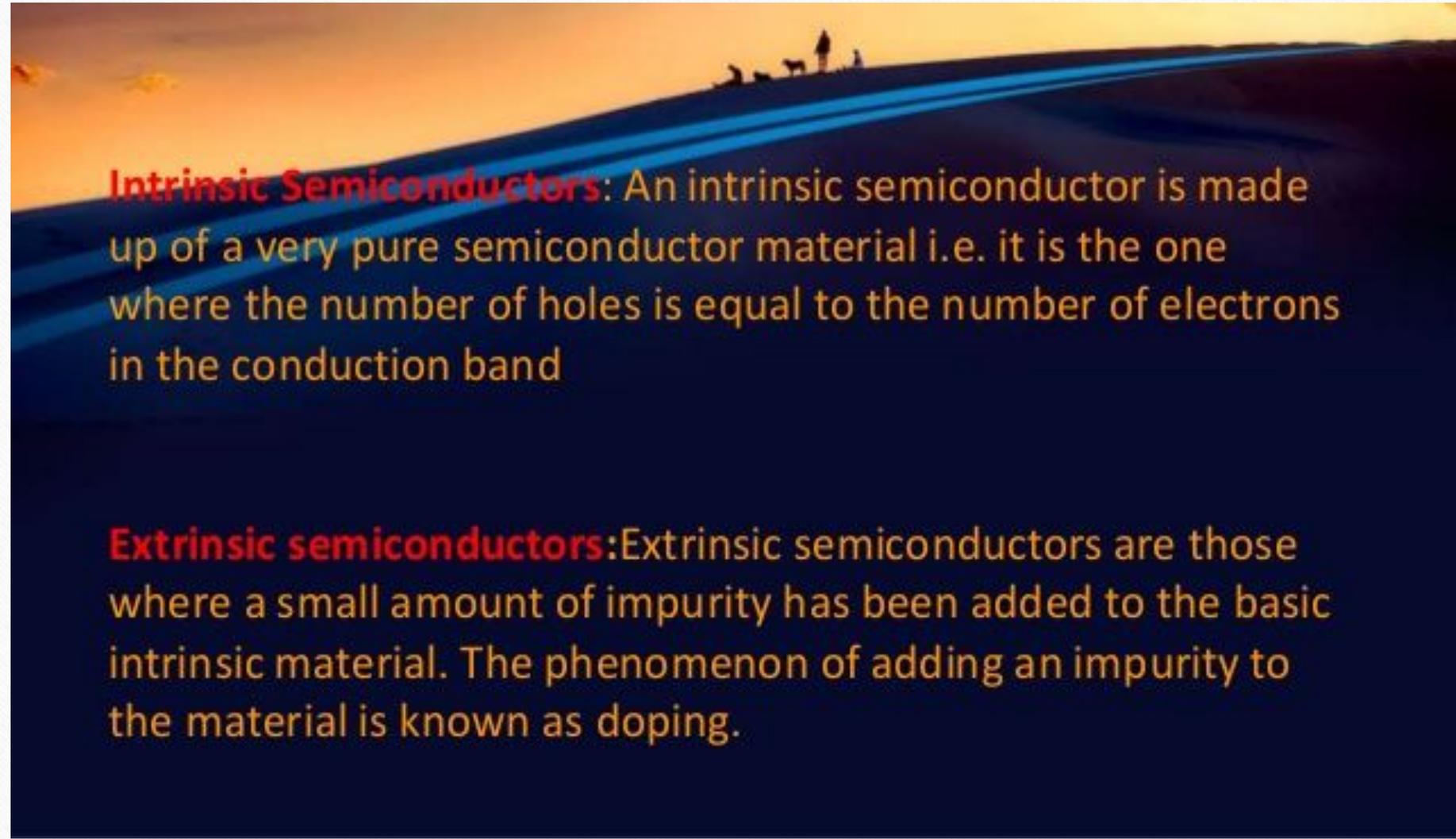
❖ N-Type Semiconductors

Donor impurities donate negatively charged electrons to the lattice, so a semiconductor that has been doped with a donor is called an n-type semiconductor; "n" stands for negative. Free electrons outnumber holes in an n-type material, so the electrons are the majority carriers and holes are the minority carriers.

❖ P-Type Semiconductors



BASIS OF DIFFERENCE	p TYPE SEMICONDUCTOR	n TYPE SEMICONDUCTOR
Density of Electrons and Holes	The electron density is much greater than the hole density. $n_e \gg n_h$	The hole density is much greater than the electron density. $n_h \gg n_e$
Energy level	The donor energy level is close to the conduction band and away from the valence band.	The acceptor energy level is close to the valence band and away from the conduction band.
Fermi level	Fermi level lies between donor energy level and the conduction band.	Fermi level lies between acceptor energy level and the valence band.
Movement of Majority carriers	Majority carriers move from higher to lower potential.	Majority carriers move from lower to higher potential.



Intrinsic Semiconductors: An intrinsic semiconductor is made up of a very pure semiconductor material i.e. it is the one where the number of holes is equal to the number of electrons in the conduction band

Extrinsic semiconductors: Extrinsic semiconductors are those where a small amount of impurity has been added to the basic intrinsic material. The phenomenon of adding an impurity to the material is known as doping.

Thanks

M.Sc. III SEM.

Photochemistry

Stark Einstein's law of photochemical Equivalence.

According to this law, one molecule is activated by the absorption of one quantum of one quantum of radiation in the primary step of a photochemical reaction.

उम्मादा रासायनिक अभिक्रिया में भाग लेने वाला प्रत्येक अणु प्राथमिक पद में केवल एक क्वांटम विकिरणों का अवशोषण कर सक्रियित अणु बनाता है।

$$E = h\nu \quad [\text{one quantum}]$$

ν = frequency of the radiation.

h = Planck's constant

$$\text{Numerical Value} = 6.624 \times 10^{-27} \text{ erg. sec.}$$

$$= 6.624 \times 10^{-34} \text{ Joule sec.}$$

$$\nu = \frac{c}{\lambda}$$

c = Velocity of light

Numerical value of

Velocity of light

$$= 3.00 \times 10^{10} \text{ cm/s}$$

$$3.00 \times 10^8 \text{ m/s}$$

$$\left[\begin{aligned} 1 \text{ \AA} &= 10^{-8} \text{ cm} \\ &= 10^{-10} \text{ m} \end{aligned} \right]$$

$$E = \frac{Nhc}{\lambda} \quad \begin{array}{l} \text{प्रति मोल ऊर्जा} \\ \text{mole energy} \end{array}$$

\Rightarrow One Einstein energy

ऊर्जा जो एक ग्राम-अणु पदार्थ द्वारा अवशोषित होती है, ऊर्जा का एक माइ-इटाशन है। जितनी तरंगदैर्घ्य जितनी ही कम होगी, उतनी ही अधिक अवशोषित ऊर्जा उतनी ही अधिक होगी क्योंकि $E \propto \frac{1}{\lambda}$.

DATE _____
PAGE _____
What is quantum yield of a photochemical reaction?

आइ-स्टॉबन का प्रकाश रासायनिक तुल्यता का नियम सही है तो प्रत्येक ग्राम अणु पदार्थ अवशोषित करता है तो पदार्थ का एक ग्राम अणु अपघटित होगा। यह सम्बन्ध अवशोषित ऊर्जा तथा उसके अपघटित पदार्थ के मध्य है। इस सम्बन्ध को स्क्वाण्टम दक्षता ϕ के रूप में व्यक्त करते हैं।

Quantum yield ϕ is defined as the number of molecules reacted per quantum of the absorbed light.

Mathematically -

$$\phi = \frac{\text{Number of molecules reacting in a given time}}{\text{Number of quanta absorbed in the same time}}$$

A photochemical reaction involves two distinct processes.

- (i) Primary process
- (ii) Secondary process.

In primary process, a molecule after absorbing one quantum of radiation may get excited or undergo dissociation to yield excited molecule.

The excited molecule/atom/free radical produced may get involved in secondary process.

Numerical Problem.

In a photochemical reaction 0.001 moles of product are formed at wavelength 4000 \AA by the absorption of light $5.0 \times 10^8 \text{ erg}$. Calculate the quantum yield.

प्रकाश रासायनिक अभिक्रिया में 0.001 मोल उत्पाद
जाने होता है। इस अभिक्रिया 4000 Å वाली
प्रकाश विकिरण का 6.0×10^8 अर्ग ऊर्जा अवशोषित
करती है। क्वाण्टम दक्षता की गणना करें।

हल - Energy of one quantum = $\frac{hc}{\lambda}$

$$= \frac{6.624 \times 10^{-27} \times 3 \times 10^{10}}{4000 \times 10^{-8} \text{ cm.}}$$

जति क्वाण्टा
ऊर्जा.

$$1 \text{ Å} = 10^{-8} \text{ cm}$$

$$E = 4.9 \times 10^{-12} \text{ Erg.}$$

$$4000 \text{ Å} = 4000 \times 10^{-8} \text{ cm}$$

$$= 4 \times 10^{-5} \text{ cm.}$$

$$\frac{\text{Number of quantum Absorbed}}{\text{Total Energy}} = \frac{\text{Energy of one quantum}}{\text{Energy of one quantum}}$$

$$= \frac{6.0 \times 10^8 \text{ erg}}{4.9 \times 10^{-12} \text{ erg}}$$

$$= 1.22 \times 10^{20}$$

$$\frac{\text{Number of molecule formed}}{\text{Total Energy}} = 0.001 \times 6.023 \times 10^{23}$$

$$\phi = \frac{0.001 \times 6.023 \times 10^{23}}{1.22 \times 10^{20}}$$

$$= \frac{6.023}{1.22} \approx 4.9 \approx 5$$

$$\boxed{\phi = 5 \text{ Ans.}}$$

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Dr Ila Jain ,Professor,Govt Dr SPM Science And Commerce
College Bhopal

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New Session Creation for Registration



Student Registration

New Registration of Student



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Session Report

Get Session Data Report



Close Session

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Enrollment Number

Get Details





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SWOT ANALYSIS

Dr Ila Jain ,Professor

Govt Dr Shyama Prasad Mukherjee Science and Commerce College Bhopal

Internal

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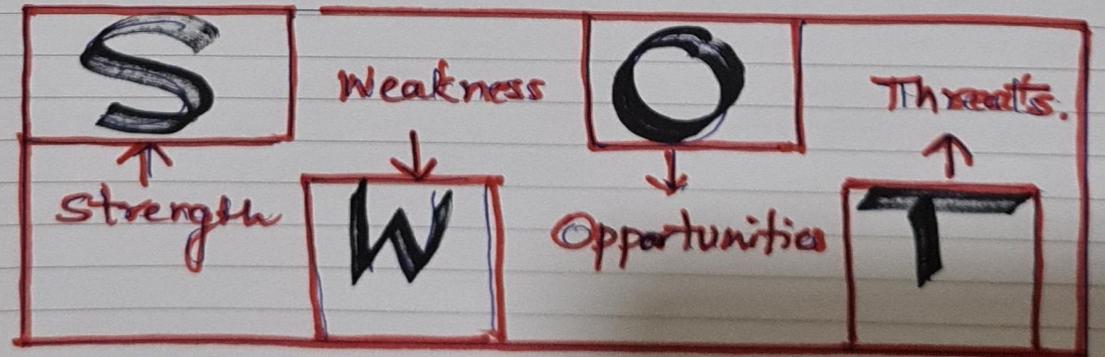
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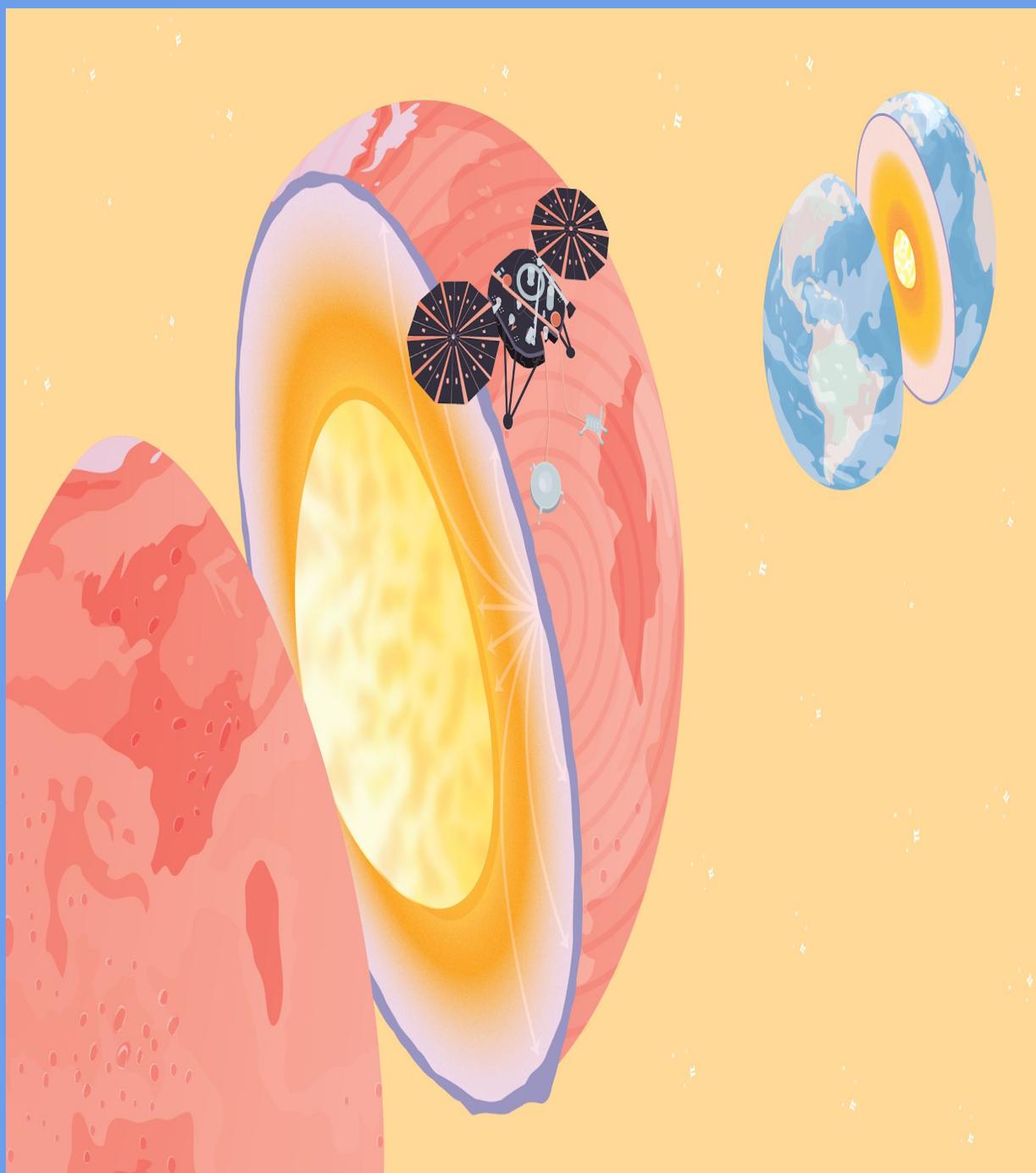
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[Personality Development]

Ex-2
SWOT ANALYSIS

1960 के दशक में क्वर्ट हर्फी द्वारा यह किया गया
 यह है इसमें

- S = Strength (ताकत)
- W = Weakness (कमजोरी)
- O = Opportunities (अवसर)
- T = Threats (खतरा, डर)

शामिल है किसी व्यक्ति या संस्था द्वारा यह जानने और
 उसके अनुसार कार्य करने के लिए यह विश्लेषण (स्कॉट)
 किया जाता है।

इसका उपयोग अपने को जानना तथा
 लक्ष्य प्राप्त के लिए स्वयं में परिवर्तन होता है। व्यक्ति
 या संस्था किसी के लिए भी यह कपातण ही
 प्रक्रिया होती है।

यह विश्लेषण करने से आंतरिक व
 बाह्य वातावरण को जाना जाता है। वह अपनी समस्त
 आंतरिक शक्तियों का प्रयोग अधिक से अधिक लक्ष्य
 ही प्राप्त करता है और विपक्षन कमजोरियों के
 उभाव को न्यूनतम करके समाप्तियों को ~~उच्च~~ उभावरण
 कर देता है।

लक्ष्य के रूप में लक्ष्य प्राप्त के
 लिए एक आवरण तथा विशेष रणनीति की आवश्यकता
 होती है जिससे निर्णय लेते समय सभी बातों को
 पहचान सके और इसी के अनुसार कार्य रेखा तैयार
 कर अपने लक्ष्य को प्राप्त किया जा सकता है। हम
 न तो अभी भी अवसरों का विश्लेषण करते हैं, ना
 ही पहचानते हैं जिससे हमारे लक्ष्य प्राप्त में
 बाधा आती है या फिर लक्ष्य से भटक जाते
 हैं।

Strength

- * What quality do I have?
- * What do I do well?
- * What is the level of my education?
- * What is my biggest achievement?
- * What personal quality do I possess?

Internal questions. Positive

Weakness

- * What am I bad in?
- * What can I improve?
- * What are my personal flaws?
- * What tasks do I usually avoid doing?
- * What are the roots of my failure?

Internal Questions. Negative

S W O T

Opportunities

- * What trends do I see in my area?
- * Can I obtain better education?
- * How can I get noticed?
- * Can I work something different?
- * Who can support me in achieving my goals?

External questions. Positive

Threats

- * What obstacles do I face?
- * Who/what may get in my way?
- * Are there any changes?
- * Am I overstable?

Internal questions. Negative

Object - विद्यार्थी अपनी SWOT Analysis करें।

नाम - X Y Z
 कक्षा - BA प्रथम वर्ष
 पारिवारिक - व्यापारिक / टुकड़ / नौकरीपेशा परिवार आई.
 प्रकृत शक्ति
 स्वयंका लक्ष्य - स्वयं का व्यापार / सरकारी नौकरी / प्रायवेट नौकरी / उच्च शिक्षा उपर से व्यवसाय स्थापित / पारिवारिक व्यवसाय में लगना. आई

आपकी ताकत

- 1. सुबह जल्दी उठना.
- 2. अपना काम स्वयं करना
- 3. बड़ों के काम में मदद करना
- 4. समय के पाबंद
- 5. दिये गये काम को समय में पूरा करना
- 6. बड़ों की बातों को सुनना और आदर करना
- 7. अपने लक्ष्य प्राप्ति के लिए संकल्पित

आपकी कमजोरी

- 1. मोबाइल फोन का अधिक प्रयोग
- 2. किताबों से प्रभावित न करना
- 3. दिये गये सीखों पर कमल न करना
- 4. आलस
- 5. बड़ों का अनादर
- 6. गुत्तसा
- 7. रात में देर से सोना
- 8. काम समय खाना
- 9. घर से बाहर भ्रमण करना.

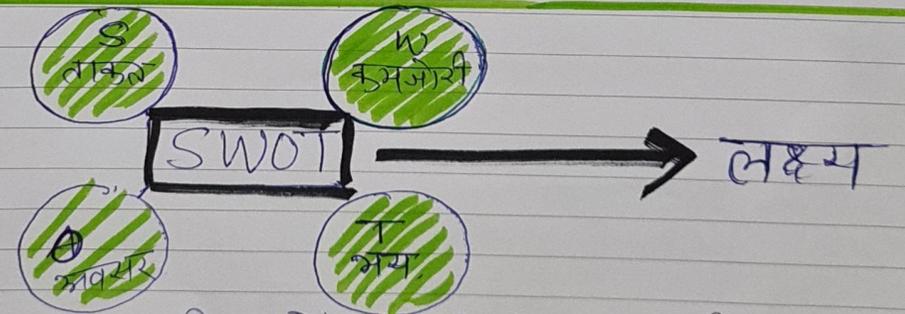


आपके लिए अवसर

- उपमश्रेणी में XA पास होने पर अच्छे महाविद्यालय में प्रवेश
- महाविद्यालय में विभिन्न सम्पन्न कार्यक्रम
- खेलकूद प्रतियोगिता / अन्य प्रतियोगिता में भाग लेने का अवसर
- विभिन्न सम्पन्न कैंप (पहले से जात कॉशिल के आधार पर) में भाग लेने का अवसर
- विभिन्न छात्रसंघों से अपनी पहचान एवं कॉशिल जात करना

आपके डर च्यमकी

- अपनी लक्ष्य जाति में स्वयंकी कमजोरी को अपने ऊपर हावी होने देना
- समय को जाति हुये देरवना
- समय की जाति के अनुसार अपने को जाति हुये न जाने पर डर कर ऊठ जाना
- अन्य लुभावने (समय) आकर्षक खेल जो समय जाया करते हैं उन से न डबर जाना
- कठिन परीक्षाये तथा प्रतियोगिता को ही ज्यादा होना



छात्र के जीवन में यह विश्लेषण इसकी लक्ष्य जाति में सहायता करता है।



Chemical Kinetics

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What is chemical kinetics

Chemical kinetics is the part of chemical science dealing with the study of the

➤ **rates of chemical reactions**
and

➤ **the factors which affect the reaction rates.**

Reaction Rates

Rate of a chemical reaction = change in concentration (mol/L) of a reactant or product with time (s, min, hr);

Rate of Reaction =
$$\frac{\text{Change in Concentration}}{\text{Change in Time}}$$

Reaction Rates and Stoichiometry



Two moles of A disappear for each mole of B that is formed.

$$\text{rate} = - \frac{1}{2} \frac{\Delta[A]}{\Delta t} \qquad \text{rate} = \frac{\Delta[B]}{\Delta t}$$



$$\text{rate} = - \frac{1}{a} \frac{\Delta[A]}{\Delta t} = - \frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

Write the rate expression for the following reaction:



$$\text{rate} = -\frac{\Delta[\text{CH}_4]}{\Delta t} = -\frac{1}{2}\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{\Delta[\text{CO}_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

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Determine the rate law and calculate the rate constant for the following reaction from the following data:



Experiment	$[\text{S}_2\text{O}_8^{2-}]$	$[\text{I}^-]$	Initial Rate (M/s)
1	0.08	0.034	2.2×10^{-4}
2	0.08	0.017	1.1×10^{-4}
3	0.16	0.017	2.2×10^{-4}

$$\text{rate} = k [\text{S}_2\text{O}_8^{2-}]^x [\text{I}^-]^y$$

$$y = 1$$

$$x = 1$$

$$\text{rate} = k [\text{S}_2\text{O}_8^{2-}] [\text{I}^-]$$

Double $[\text{I}^-]$, rate doubles (experiment 1 & 2)

Double $[\text{S}_2\text{O}_8^{2-}]$, rate doubles (experiment 2 & 3)

$$k = \frac{\text{rate}}{[\text{S}_2\text{O}_8^{2-}][\text{I}^-]} = \frac{2.2 \times 10^{-4} \text{ M/s}}{(0.08 \text{ M})(0.034 \text{ M})} = 0.08/\text{M}\cdot\text{s}$$

14



RATE OF REACTION

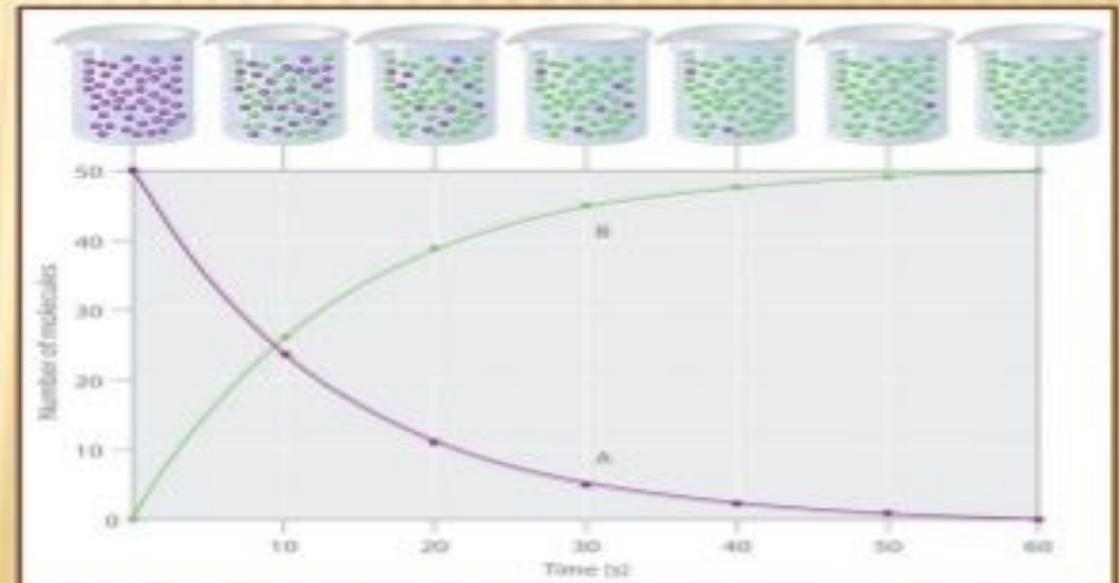
Rate Of Reaction

Change in the concentrations of reactants or products per unit time

Progress of a simple reaction,



- Concentration of Reactant A (purple) decreases with time*
- Concentration of Product B (Green) increases with time*
- Concentrations of A & B are measured at time t_1 & t_2 respectively A_1, A_2 & B_1, B_2*



The graph shows the change in the number of A and B molecules in the reaction as a function of time over a 1 min period (bottom)



FACTORS AFFECTING THE RATE

F
A
C
T
O
R
S

Nature Of Reactants

Surface Area Of Reactants

Concentration Of Reactants

Temperature

Catalyst

Nature Of Reactants

- Rate of "**Homogeneous Reactions**" is higher than the "**Heterogeneous Reactions**"
- Rate depends on the physical state of reactants , e.g. liquid /gaseous/solid
- Rate depends on the number of collisions or encounters between the reacting species

Surface Area Of Reactants

- **Heterogeneous** reaction occurs at interface of two phases of reactants
- If one reactant is **Solid**, rate increases with increase in surface area of solid phase reactant
- Surface area increases, area of contact between reactants increases - rate of encounter between reactants increases - **Rate** increases
- Surface area of a solid can be increased by **Sub-division** i.e. dividing the bigger particles in smaller



The same mass of Steel wool bursts into flame



A Hot Steel nail glows feebly when placed in oxygen

CONTINUED



Reaction Order "n"	Rate variation with Conc.	Differential Rate Law	Integrated Rate Law
1	Rate doubles when [A] doubles	Rate = $k [A]^1$	$\ln [A]_t / [A]_o = -kt$
2	Rate quadruples as [A] doubles	Rate = $k [A]^2$	$1/[A]_t = kt + 1/[A]_o$
0	Rate does not change with [A]	Rate = $k [A]^0$	$[A]_t - [A]_o = -kt$



$[A]$ versus Time plot for 0, 1st & 2nd order rxns



Rate versus $[A]$ plot for 0, 1st, 2nd order rxns



Rate Law : $k[\text{NO}]^2[\text{H}_2]$

Order of reaction = 3

1st Order wrt $[\text{H}_2]$
2nd Order wrt $[\text{NO}]$

Stoichiometric coefficient of $[\text{H}_2] = 2$
Order with respect to $[\text{H}_2] = 1$

Reaction orders must be determined from experimental data and cannot be deduced from the balanced equation

Method for determining
Order of reaction

Half Life
Method

Powell Plot
Method

Isolation
Method

Initial Rate
Method

Summary of the Kinetics of Zero-Order, First-Order and Second-Order Reactions

Order	Rate Law	Concentration-Time Equation	Half-Life
0	rate = k	$[A] = [A]_0 - kt$	$t_{1/2} = \frac{[A]_0}{2k}$
1	rate = $k [A]$	$\ln[A] = \ln[A]_0 - kt$	$t_{1/2} = \frac{\ln 2}{k}$
2	rate = $k [A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$t_{1/2} = \frac{1}{k[A]_0}$

First-Order Reactions

The **half-life**, $t_{1/2}$, is the time required for the concentration of a reactant to decrease to half of its initial concentration.

$$t_{1/2} = t \text{ when } [A] = [A]_0/2$$

$$t_{1/2} = \frac{\ln \frac{[A]_0}{[A]_0/2}}{k} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

What is the half-life of N_2O_5 if it decomposes with a rate constant of $5.7 \times 10^{-4} \text{ s}^{-1}$?

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{5.7 \times 10^{-4} \text{ s}^{-1}} = 1200 \text{ s} = 20 \text{ minutes}$$

How do you know decomposition is first order?

units of k (s^{-1}) ¹⁸

The reaction $2\text{A} \longrightarrow \text{B}$ is first order in A with a rate constant of $2.8 \times 10^{-2} \text{ s}^{-1}$ at 80°C . How long will it take for A to decrease from 0.88 M to 0.14 M ?

$$\ln[A] = \ln[A]_0 - kt \quad \begin{array}{l} [A]_0 = 0.88 \text{ M} \\ [A] = 0.14 \text{ M} \end{array}$$

$$kt = \ln[A]_0 - \ln[A]$$
$$t = \frac{\ln[A]_0 - \ln[A]}{k} = \frac{\ln \frac{[A]_0}{[A]}}{k} = \frac{\ln \frac{0.88 \text{ M}}{0.14 \text{ M}}}{2.8 \times 10^{-2} \text{ s}^{-1}} = 66 \text{ s}$$

First order reactions

Let's add another result ...

[X] mol dm ⁻³	[Y] mol dm ⁻³	Rate mol dm ⁻³ s ⁻¹
0.01	0.02	0.0004
0.01	0.04	0.0008
0.005	0.04	0.0004

Question ...

What is the order of X?

1

So, the overall rate equation is ... **rate = k[X][Y]**

Question ...

What is the value of the rate constant?

$$k = \frac{\text{rate}}{[X][Y]} = \frac{0.0004}{0.01 \times 0.04} = \underline{1.0 \text{ mol}^{-1} \text{ dm}^{-3} \text{ s}^{-1}}$$

Units of k

The units of the rate constant (k) vary depending on the order of the reaction ...

First order reaction

$$\dots \text{ rate} = k[A]$$

$$\begin{array}{l} \text{rate (mol dm}^{-3} \text{ s}^{-1}) \\ [A] \text{ (mol dm}^{-3}) \end{array}$$

$$\cancel{\text{mol dm}^{-3}} \text{ s}^{-1} = k \times \cancel{\text{mol dm}^{-3}}$$
$$\text{s}^{-1} = k$$

Second order reaction

$$\dots \text{ rate} = k[A][B]$$

$$\begin{array}{l} \text{rate (mol dm}^{-3} \text{ s}^{-1}) \\ [A] \text{ \& [B] (mol dm}^{-3}) \end{array}$$

$$\cancel{\text{mol dm}^{-3}} \text{ s}^{-1} = k \times \cancel{\text{mol dm}^{-3}} \times \cancel{\text{mol dm}^{-3}}$$
$$\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1} = k$$



MOLECULARITY

Molecularity

Number of colliding molecular entities that are involved in a single reaction step

Unimolecular



Bimolecular



Termolecular



Molecularity	Elementary Step	Rate law	Examples
Unimolecular	$A \longrightarrow \text{Products}$	$\text{rate} = k [A]$	$N_2O_4(g) \longrightarrow 2NO_2(g)$
Bimolecular	$A + A \longrightarrow \text{Products}$ $A + B \longrightarrow \text{Products}$	$\text{rate} = k [A]^2$ $\text{rate} = k [A][B]$	$2NOCl \longrightarrow 2NO(g) + Cl_2(g)$ $CO(g) + NO_3(g) \longrightarrow NO_2(g) + CO_2(g)$
Termolecular	$A + A + A \longrightarrow \text{Products}$ $A + A + B \longrightarrow \text{Products}$ $A + B + C \longrightarrow \text{Products}$	$\text{rate} = k [A]^3$ $\text{rate} = k [A]^2 [B]$ $\text{rate} = k [A][B][C]$	$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ $H + O_2(g) + M \longrightarrow HO_2(g) + M$

<i>Molecularity</i>	<i>Order</i>
<ul style="list-style-type: none">• <i>Number of reacting species which collide to result in reaction</i>• <i>Only positive integral values e.g 1,2,3 & never -ve</i>• <i>Theoretical concept & value is derived from mechanism of reaction</i>	<ul style="list-style-type: none">• <i>Sum of powers to which concentrations are raised in the rate law expression</i>• <i>Zero, fractional or even be -ve</i>• <i>Experimental fact & derived from rate law</i>

*Rate
Determining
Step*

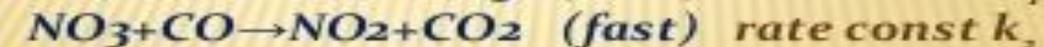
*Slowest step of a
chemical reaction
that determines the
speed (rate) at
which the overall
reaction proceeds*



Eg: A complex reaction



occur in two elementary steps :



$$\text{Rate} = k_1 [\text{NO}_2][\text{NO}_2] = k_1 [\text{NO}_2]^2$$

Temperature and k

Because k varies with temperature it can be used to compare the same reaction at different temperatures

Temperature (K)	Rate Constant ($\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$)
633	0.0178×10^{-3}
666	0.107×10^{-3}
697	0.501×10^{-3}
715	1.05×10^{-3}
751	15.1×10^{-3}



This only works if the concentration of the reactants remains the same

Question ...

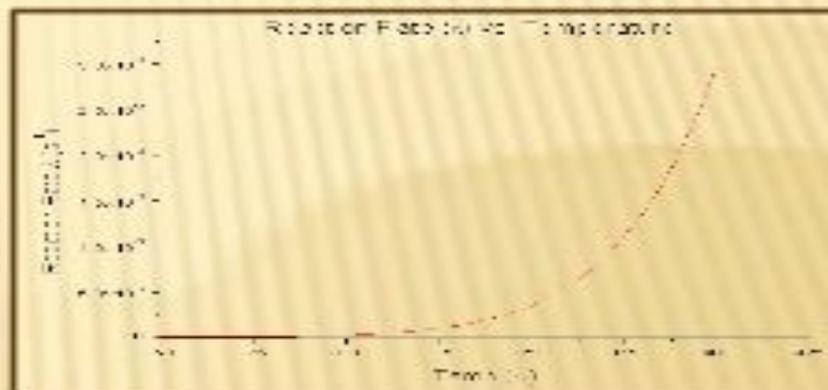
What can we deduce from the table?

As temperature increases so does the value of k



CONTINUED

- *Temperature dependence is expressed by - Arrhenius Equation*
- *Rate increases non linearly with temperature as shown in graph, k increases exponentially as T increases :*



Arrhenius Equation

$$k = Ae^{-E_a/RT}$$

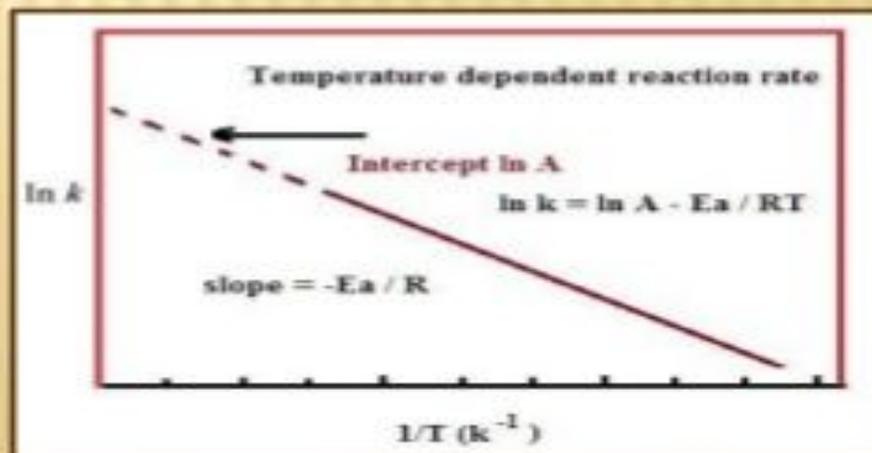
k = rate constant
A = frequency factor
 E_a = activation energy

Taking log

$$\ln k = \ln A - E_a / RT$$

Activation Energy

Minimum energy required to initiate a chemical reaction



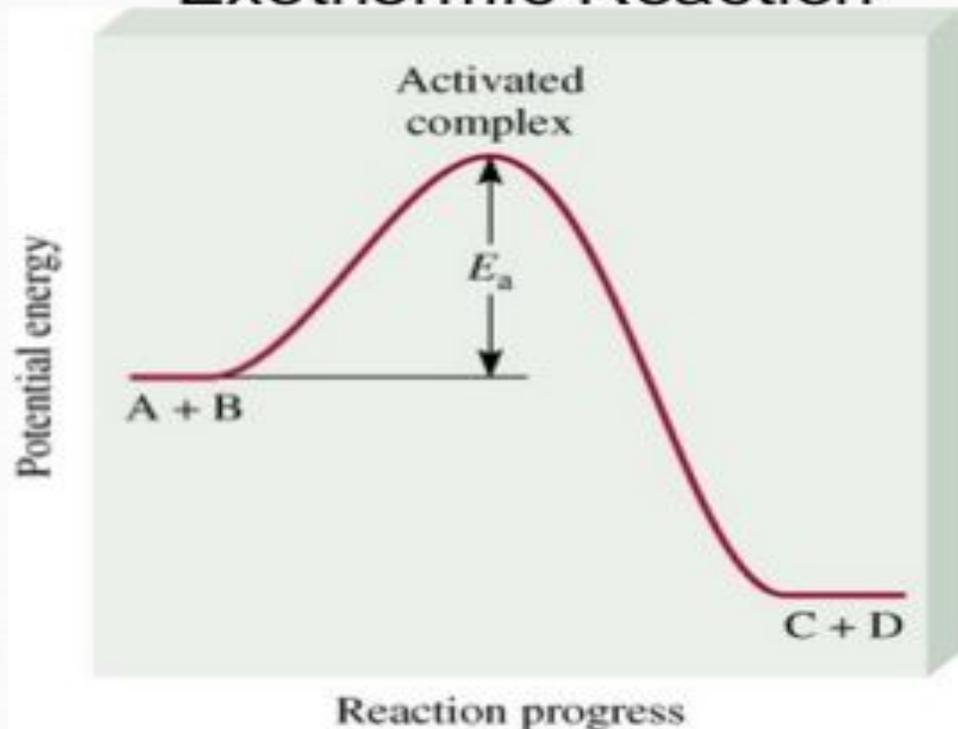
Arrhenius Plot

Higher T \longrightarrow Larger k \longrightarrow Increases Rate

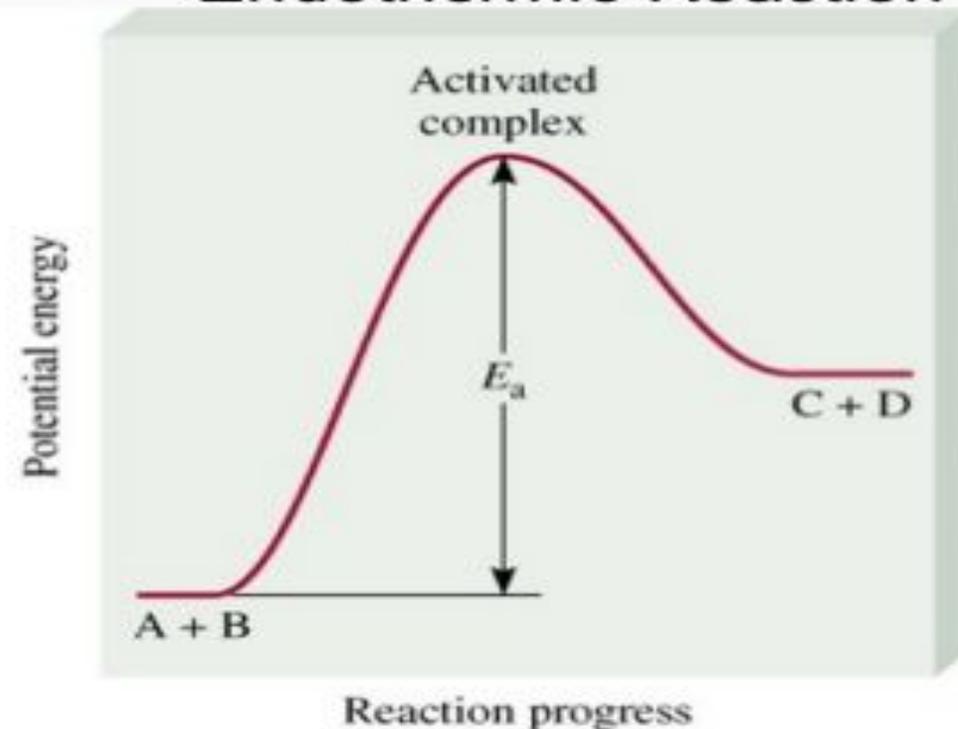
Smaller E_a \longrightarrow Larger k \longrightarrow Increases Rate



Exothermic Reaction



Endothermic Reaction



The **activation energy** (E_a) is the minimum amount of energy required to initiate a chemical reaction.

Alternate Form of the Arrhenius Equation

At two temperatures, T_1 and T_2

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

or

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{T_1 - T_2}{T_1 T_2} \right)$$



chemical-kinetic 2.pdf