Aliphatic Hydrocarbons

Hydrocarbon

A compound of carbon and hydrogen is known as hydrocarbon.

• Saturated Hydrocarbon

A hydrocarbon is said to be saturated if it contains only C—C single bonds.

For example: Ethane CH₃—CH₃

• Unsaturated Hydrocarbon

A hydrocarbon is said to be unsaturated if it contains C = C or C = C multiple bonds. Example: ethene $CH_2 = CH_2$

ethyne HC≡CH

• Aromatic Hydrocarbon

Benzene and its derivatives are called aromatic compounds.

Alkanes

Alkanes are the simplest organic compounds made of carbon and hydrogen only. They have the general formula C HC_{n-2} (where n = 1, 2, 3 etc.)

They have the general formula C_nHC_{2n+2} (where n = 1, 2, 3, etc.)

The carbon atoms in their molecules are bonded to each other by single covalent bonds. Since the carbon skeleton of alkanes is fully saturated' with hydrogens, they are also called saturated hydrocarbons. Alkanes contain strong C —C and C —H bonds. Therefore, this class of hydrocarbons are relatively chemically inert. Hence they are sometimes referred to as paraffins (Latin parum affinis = little affinity). First three members of this class can be represented as





Structure of methane

In methane carbon forms single bonds with four hydrogen atoms. All H—G—H bond angles are of 109.5°. Methane has a tetrahedral structure. C—C and C—H bonds are

formed by head-on overlapping of sp³ hybrid orbitals of carbon and Is orbitals of hydrogen atoms.

Preparation of alkanes

- 1. Naturally, they are synthesised by decomposition of plants and waste matter.
- 2. In laboratory: They are prepared from :
 - From unsaturated hydrocarbons
 - From alkyl halides
 - By reduction of alkyl halides
 - By use of Grignard reagent
 - From carboxylic acids

(a) **From unsaturated Hydrocarbons**:-The method involved is by hydrogenation that is addition of H_2 . It is also called as reduction reaction. The general reaction involved:

ethene

hydrogen

ethane

A Special reaction occurs where we use Raney Ni which is actually activated nickel (alloy of 50 % Ni, 50 % Al). But the reaction is assigned a special name that is **Sabatier Sanderson Reduction.** The reaction is given below:

$$\begin{array}{c} CH_{z} = CH_{z} + H_{z} \\ (ethene) \end{array} \xrightarrow{\text{Raney Ni}} CH_{a} - CH_{a} \\ (Ethane) \end{array}$$

(b) From Alkyl halides (RX)

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The methods that can be used for preparing alkanes by using alkyl halides are:

- Wurtz reaction
- Reduction of alkyl halide
- By use of Grignard reagent
- **Wurtz reaction**: in this two molecules of alkyl halide react with sodium in presence of dry ether as shown below:

Please note the dry ether is used so as to keep sodium dry so that it does not catch fire in moist conditions.

Limitation of this reaction: is that we need to take same alkyl halides otherwise we get mixtures of alkanes and due to almost same boiling points etc, they are difficult to separate. Another limitation of this is that by this method we can prepare alkanes only with even number of Carbon atoms.

(c) **Reduction of alkyl halides**: - It can be done by using various Reducing agents like:

• With Zn and HCl

In this the Zn and HCl both react and produce nascent Hydrogen to carry out reduction.

(Zn/HCl)

CH₃CH₂X + 2H₂ --> CH₃CH₃ + HX (Ethyl halide) (Ethane) (Hydrogen Halide)

• Pt or Pd can be used as reducing agent

(Pt/Pd)CH₃CH₂Br + H₂ --> CH₃CH₃ + HBr

(d) By use of Grignard reagent (RMgX)

RX + Mg dry ether RMgX CH₃CH₂ Br + Mg dry ether CH₃ CH₂MgBr (Ethyl brom ide) (ethyl magnesium bromide) Then its hydrolysis is carried out : CH₃ CH₂ MgBr + H₂ O → CH₃CH₃ + Mg (OH)Br (ethane) (magnesium hydroxyl bromide)

(d) From Carboxylic acids (RCOOH)

 $_{\odot}$ **By Decarboxylation:** It is removal of of CO₂ In this first carboxylic acid, is made to react with sodium metal then followed by its reaction with sodium hydroxide to get the desired alkane.

 $\begin{array}{rl} \mathsf{CH}_3 \operatorname{COOH} + \operatorname{Na} & \rightarrow \mathsf{CH}_3 \mathrm{COONa} + \operatorname{H}_2 \\ & (\text{sodium acetate}) \\ \mathsf{CH}_3 \mathrm{COONa} + \operatorname{Na} \mathrm{OH} & \rightarrow & \mathsf{CH}_4 + \operatorname{Na}_2 \mathrm{CO}_3 \\ & (\text{Soda lime}) \end{array}$

• **Kolbe's electrolysis Reaction:** In this electric current is passed through metal carboxylic salt

 $CH_{3}COONa + H_{2}O \qquad electricity C_{2}H_{6} + NaOH + CO_{2} + H_{2}$

Chemical properties of alkanes

We know that on saturated Hydrocarbons are quite less reactive and undergo reaction with difficulty therefore they are called paraffin's.

The reactions shown by them are given below:

- 1st **Substitution reaction**: In this one or more Hydrogen's are replaced by other atoms.
- For example
- Halogenations In it the Substitution By halogen X (Cl, F, Br, I) occur
 Order of reactivity: F> Cl > Br > I

Out of them chlorine shows this reaction to an efficient level.

Chlorination of methane: This reaction occurs in normal light



• **2nd Oxidation Reaction**: it is the Reaction with oxygen

This reaction may be may be uncontrolled or controlled oxidation. If it is combustion reaction than the products are always CO_2 , H_2O , heat and light.

• If it is Complete combustion : then also the products are CO₂, H₂O, heat and light

 $CH_4 + O_2 - CO_2 + H_2O + Heat$

• Incomplete combustion or oxidation :

 $CH_4 + O_2 \longrightarrow CO + H_2O + Heat$

This CO makes the surface block and called Carbon black or soot.

 Controlled oxidation - occur in presence of catalyst and on the basis of catalyst the products are formed. Like in presence of Copper alcohol is formed, in presence of molybdenum oxide – aldehyde is formed and in presence of silver oxide –carboxylic acid is formed.



o 3rd Isomerisation

If we subject alkanes to (anhydrous) Aluminium chloride then isomer of alkane is formed.



4th Aromatization Reaction: In this an Aromatic compounds are found are called (Cyclization)



• **5th Thermal decomposition or pyrolysis**: In this breakdown of bigger alkane into lower alkanes occur and is called as thermal cracking.



Alkenes

They are the hydrocarbons with C = C (double bond) with one sigmabond and other pi bond.

- $_{\circ}$ $\,$ Their General formula $\,$ C_{n} H_{2n}
- They are oil like called olefins.
- $_{\odot}$ They are reactive due to π bond and common reaction they undergo in addition Reaction

The lowest member of alkenes is ethene (C_2H_4) .



• The structure of alkene is:

1. **From alkyl halides: (RX)** by the process of dehydrohalogenation, it is also called Beta elimination .



In this case it has two beta carbons so, we make use of special rule that is Saytzeff's rule.

Saytzeff's rule: In case of reacting alcoholic KOH with unsymmtrical halide , that alkene is preffered which is maximum alkylated. So , in above example But -2 - ene is preferred . If we see ease of elemination the order is :

I > Br > Cl > F

The better the leaving group more easily the reaction occurs .The reactivity of alkanes towards this reaction is : tertiary > secondary > primary

2. From dihalogen derivatives

Let us take an example of Vicinal dihalide that is :

In this renewal of halogen is taking place therefore the process is called dehalogenation .

3. **From alkynes :** by the process hydrogenation. The reaction involved is given below:



4. From Alcohols :

It is prepared by Dehyration Reaction of alcohols.

$$\begin{array}{c|c} CH_3 - CH_2 & \hline Concentrated & CH_2 = CH_2 \\ & & H_2 SO_4 \\ & OH \\ (ethanol) & (ethene) \\ The ease of Reaction is: $3^0 > 2^0 > 1^0 \end{array}$$$

The ease of Reaction is: $3^0 > 2^0 > 1^0$ Another example is:



Chemical properties of alkenes

It shows mainly two types of reactions:

- Electrophilic addition reaction :
- Oxidation reaction

1. Electrophilic addition reactions

The basic mechanism involved in it is shown below:



• Addition of halogen

 $CH_2 = CH_2 + Br_2$ CCL₄ UH2 ethene bromine Br Br 1, 2 dibromo ethene

Order of reactivity of halogens towards this reaction is:

 $F_2 > Cl_2 > Br_2 > I_2$

- In case of addition of fluorine, the reaction occurs so violently that it leads to explosion, as it is an exothermic reaction.
- In case of addition of iodine, the reaction take place under special conditions as the reaction is reversible.
- This reaction is also considered as a test for un-saturation (alkenes and alkynes): bromine water test. This test is given below.

(Test for un-saturation)

CH3 - CH2	= CH _z + Br _z	CCL	-	CH₃ CH -	CH _z
					1
propene	bromine			Br	Br
(Dark Brown		1,2 dibromo propane			
Liquid)		(colourless)			

• Addition of halogen acids (HX)

The order of reactivity towards this reaction is:

st s-	st s-	St 5-	St 5-
HF	< HCl	< HBr <	Hi

• The HI has weak bond because of incomparable size, that is the reason its reactivity is high towards this reaction.

In case of unsymmetrical alkenes, Markovnikov's rule is followed.

- Markovnikov's rule: According to this, addition of any group in unsymmetrical alkene, the negative part of the reagent will attach itself to the Carbon atom carrying lesser number of Hydrogen and Hydrogen goes to the Carbon with maximum number of hydrogen.
- But if Reaction occurs in presence of peroxide like benzoyl peroxide, The rule that is followed is Anti-Markovnikov's Rule or Kharasch effect (and this valid only for HBr).
- **Anti Markonikovs Rule** :According to it the negative part attaches to the carbon atom with maximum number of hydrogen and positive part attaches to the carbon atom with lesser hydrogen .

CH₃ - CH = CH₂ + HBr <u>benzoyl</u> CH₃ - CH₂ - CH₂ Br propene Peroxide Bromo propane hydrogen bromide

- Mechanism involved is free radical mechanism as shown below :
- Chain initiation step:

 $C_{c}H_{3}COOC_{c}H_{3} \rightarrow C_{c}H_{3}COO^{\circ} + C_{c}H_{3}COO^{\circ}$ phenyl free radical!

This radical is unstable therefore it decomposes to form $C_6 H_5^*$ (Phenyl free radical) and $CO_{2.}$

• Chain Propagation step:



We know 2^o free radical more stable therefore, the preferred product is going to be that which helps in yielding 2^o free radical. Please note:

- Markonikov's Rule is for all attacking agents.
- Anti-Markonikov's Rule is only for HBr (due to thermodynamic reasons).

Rearrangement of Carbocation – Hydride shift



Which is maximum (stable).

(d)Addition of H₂O



2. Oxidation Reactions The oxidation can occur in different ways: Combustion

Complete oxidation: In this CO₂, H₂O, heat and light is produced

Incomplete combustion: In this CO, H₂O and heat and light are given out. **Controlled oxidation**: It occurs in different ways:

 Oxidation with (cold & dilute) KMnO₄: Whenever oxidation of alkenes occurs in presence of strong oxidising agent like potassium permanganate. In it hydroxylation occurs and as a result alcohols (diols) are formed.

For example:

 $\begin{array}{c} CH_2 = CH_2 + [O] \xrightarrow{KMnO} HO - CH_2 - CH_2 - OH \\ ethene nascent Oxygen \\ CH_3 - CH = CH_2 + [O] \xrightarrow{} CH_3 - CH - CH_2 \\ & & & & & \\ (Propene) OH OH \\ \end{array}$

 Oxidation with hot and concentrated KMnO₄: When alkenes react with hot and concentrated potassium permanganate, the cleavage occur across double bond : For example:



Please note: If there is no Hydrogen atom with carbon connected by double bond than ketone is formed and If there is H with carbon, then carboxylic acid is formed.

• Oxidation with ozone: It is also called as ozono-lyses.



Alkynes

In this triple bond is present between carbon atoms (C C bond). The hybridisation is sp and the general formula involved is $C_nH_{2n\ -2.}$

- The lowest member of alkynes is: simplest compound that is CH CH (ethyne).
- The common name of it is acetylene.
- It has high Bond dissociation energy, as there is triple bond present therefore the energy is high of the order 823 KJ/mol.
- $_{\odot}$ Due to this reason the acetylene is mixed with O_2 and the flame is used for welding purpose.

Preparation of Alkynes

1. Laboratory preparation –It is prepared in by action of H_2O on Calcium carbide i.e. $\ensuremath{\text{CaC}_2}$

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CaC_2 + H_2O \rightarrow Ca(OH_2) + CH \equiv CH
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2. By dehydrohdogenation of vicinal dihalide

3By action of Zinc on Tetra halogen derivatives



3. We can prepare higher alkyne from acetylene: This is also called up-gradation reaction.



Chemical properties of alkynes

1. Acidic Character – This is shown by replacement of one of the hydrogen atom by metal atom.

 $CH = CH + Na \rightarrow CH = CNa + H^{+}$ ethyne sodium Acid Acetylide

Alkynes are acidic because of sp hybridisation of Carbon atom. The "s" character in case of alkynes is 50%. Due to more "s" character, electrons in sp hybrid orbitals are held more tightly by nucleus and are quite electronegative. As a result, the H - C bond get more displaced towards carbon atom and proton is easily released. Due to this, the bond easily breaks and the Hydrogen is easily released.

Application: By this we can upgrade number of carbon atoms in alkynes.

2. **Addition reaction:** The basic general reaction involved in addition is similar to that of alkenes as shown.



• Addition of halogens



• Addition of halogen acids (hydro halogenations Reaction) : The order of reactivity of this reaction is:

HF < HCl < HBr < HI

The reaction involved is:

 $\mathsf{CH} \equiv \mathsf{CH} + \mathsf{HC} \longrightarrow \mathsf{CH}_2 = \mathsf{CHC} \longrightarrow \mathsf{HC} \longrightarrow \mathsf{CH}_3 - \mathsf{CH} \mathsf{Cl}_2$

Ethyne hydrogen chloride

Gem dihalide



Anti-markoniov's rule is followed in case of addition of HBr:

Addition of H₂O (hydration Reaction) \circ



Addition of H₂ 0

Ni CH₂ = CH₂ CH =CH + H₂ Ethyne ethene

Please note:

When we use lindlar catalyst that is Pd/BaSO₄ we get Cis form and whenever we use catalyst that is Na in liquid NH₃, then it is called birch reduction and we get trans form as shown below :



2. Oxidation of alkynes

The oxidation is carried out with:

- Cold and dilute alkaline potassium permanganate
- Hot and concentrated potassium permanganate
- With ozone

With Hot and Concentrated KMnO₄



 Please note that if we carryout oxidation of butyne with acidic potassium permanganate under low and high temperature we get different products as shown below:

	- o	
CH ₃ CH ₂ COOH + CO ₂ + H ₂ O propanoic acid carbondioxid	$\begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $	→ CH ₃ CH ₂ C-Ö-O-H

With Ozone



2. Polymerisation

CH₂ Cl₂ $CH = C - CH = CH_2 \rightarrow$ $CH_2 = CH - C = C - CH_3$ 2CH = CHethyne Vinyl acetylide pent 2,4 diene Cyclic Polymerisation 0 CH 11 CH CH CH CH 11red hot riangle11

Problems

- 1. Write short note on Wurtz reaction, Kolbe's synthesis, Birch reduction, Markownikoff's and anti-Markownikoff's addition, ozonolysis, oxymercuration-demercuration and hydroboration-oxidation reaction.
- 2. How will you convert
 - i. Methyl chloride to ethane
 - ii. Ethylene to ethylene glycol
 - iii. Ethanol to erhylene
 - iv. Acetylene to propyne

SUGGESTED READINGS/REFERENCES:

Finar, I. L, Organic Chemistry (Volume 1)