General chemistry

unit - I

d - Block & f - Block elements

1.1. General characteristics of d - block elements comparative study of Zinc group elements, extractions of Mo & pt - Allow of copper, amalgams and galvanization

Evidences for the existance of Hg_2^{2+} ions

1.2. General characteristics of f - block elements. lanthanide contraction and its consequences Extraction of Th

1.3. Arrhenius, lowry - Bronsted and lewis concepts of acids and bases.

unit - II

chemistry of Organometallic Compounds.

2.1. Introductions - preparations of Organometallic compounds - physical and chemical properties - uses Organic Compounds - General properties preparations and uses.

2.2. Organolithuim, organocopper, compounds - preparation properties and uses.

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2.3 . Organolead , Organophosphorous and Organoboron compounds - preparations properties and uses .

Unit - III

Chemistry of Alcohol , phenols and Ethers .

3.1 . Nomenclature - industrial source of alcohols - preparations of alcohols ; Hydration of alkenes, oxymercurations , Hydroboration , Grignard additions reduction - physical properties - chemical properties - Uses - glycols , from dihydroxylation reductions , substitution reaction and glycerols and their uses .

3.2 . preparation of phenols including di - and trihydroxy phenols , physical and chemical properties . Uses . aromatic electrophilic Substitution Mechanisum - theory of orientation and reactivity

3.3 preparation of Ether ; dehydration of alcohols, Williamson's Synthesis - Silyl ether epoxides from peracids - Sharpes's asymmetric epoxidation reactions of epoxides - Uses - Introduction to Crown ethers - structures - applications

Thermodynamics - I.

4.1 Definitions - systems and surrouding isalated, closed and open system - state of the system - Intesive and extensive Variable Thermodynamic processes - reversible and irreversable isothermal and adiabatic process - state path functions

4.2 Work of expansion at constant pressure and at constant Volume. First law of Thermodynamic - statement - definition of internal energy (E) Enthalpy (H) and Heat capacity, Relationship between cp and cv.

4.3. Calculation of w.q dE and dH for expension of ideal and real gases Under isothermal and adiabatic conditions of reversible and irreversible process.

4.4 Thermochemistry - relationship between enthalphy of reactions at constant Volume (qv) and at constant pressure (p) - temperature dependence of head of reaction - Kirchoff's equation bond energy and its calculation from Thermochemical data - integral and differential Heats solution and dilution

Unit -V

Chemical Kinatices.

5.1. Rate of reaction - rate equations. Order and molecularity of reaction - Rate laws - Rate constants and characteristics of Zero Order, First order and second order reactions - derivation of time for half change t1/2 with example.

5.2 Methods of determination of order of reactions - experimental of methods - determination of rate constant of a reaction by Volumentry colorimetry and polarimetry

5.3 effect of temperature on reactions rate - concept of activation energy - energy barrier Arrhenius equations. Theories of reactions rates - collision theory - det: derivations of rate constant of bimolecular reactions failure of collision theory Lindemann's theory of Unimolecular reactions.

5.4. Theory of absolute reactions rates - derivation significate of rate constant for a bimolecular reactions significate of entropy and free energy of activation Comparision of collision of theory and absolute reaction rate theory (ARRT)

Unit - IV

Thermodynamics.

Thermodynamics definations

Intensive Variable

Extensive Variable.

Extensive Variable:

properties whose Value depens on the amount of the meterial present in System are called extensive properties.

Ex. Volume, Mass, entropy, Heat capacity

Intensive Variablo:

A properties whose Value don't depend on the amount of meterial present in the System are called Intensive properties

Ex. Boilling point, Freezing point, Molar Volume, Viscocity

Types of System:

It classified three types

* Isolate System

* closed System

* open System

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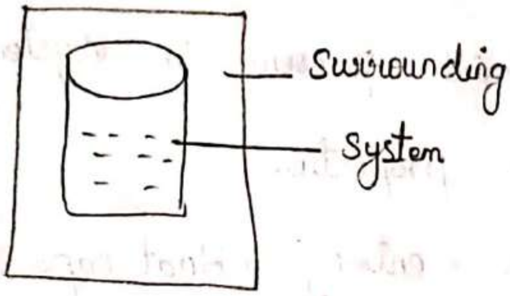
System

A system is define as any particular part of the Universe about which we are interested

The rest of the Universe is called Surroundings

Isolated System :



The System which can exchange neither energy nor - matter with its Surrounding is called an Isolated System.

Ex : To Take an ~~sy~~ example consider a closed Vessel containing water which is in contact with Vappour The Vessels is closed No Matter can leave enter the Veseles.

closed System :

A System which can exchange energy But not matter with its Surroundings is called closed System.

open System :

A System which can exchange both matter and energy with its Surroundings is called a open System.

Thermodynamic process

* cyclic process
* Reversible process
* Irreversable process.

cyclic process :-

When a System after completing a Serious changes. written to its orginal state it is said to have completed a cycle Such a process is know as cyclic process.

Reversable process

A Thermodynamicly Reverable process is a process which is carried out Infinitesimally. Slowly show that the driving force is only infinitesimally greater that opposive Force.

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Irreversable process.

On irreversable process is a process which doesn't take infinitesimally.

Difference between Reversible and irreversable :

Reversible	irreversible.
It is slow process	It is measurable process
Driving Force of a reaction only infinitesimally grater than then the opposing force	Driving Force is usually consider larger than the oppsive Force.
It proceeds in both direction	It proceeds only one direction
Workdone is greater	Workdone is less.
can be brought back to intial state	can't be brought back to be intial state.

Isothermal process :

A process said to be isothermal the temperature of the System remains Constant During each step of process.

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Suppose, a process say a chemical reaction is carried out vessels which is not insulated the System in thermal equilibrium, with the Surrounding if the process exothermic, heat is evolved in the process. The Heat is given out the Surroundings instaneously therefore the temperature of the System remains unchanged.

On other hand the reaction is endothermic, The heat observed instaneously from the Surroundings the given again the temperature of the System, remains Unchanged Such a System is called isothermal process.

Adiabatic process.

A process is said to be Adiabatic If no heat enteres or leaves the System. during any step of the process. Suppose a process say a chemical reaction is carried out in an isulated vessels.

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In this Case, No Heat can leave or enter the Vessels from the Surroundings. If the process is exothermic a heat evolved remain the System therefore the temperature of the system rises.

In other hand the process in endothermic the head is observed from the System, therefore the Temperature of the System falls. Such a system is called adiabatic System and process is called adiabatic process

State and path function:

A state function are Variables (P, V, T) which are determined only by the intial and Final state of the System and not by the path followed during the change initial to Final state

First law of Thermodynamic :

Difference forms of energy .

- * Kinetic energy
- * patentional energy.
- * chemical energy.
- * Nuclear energy.
- * electrical energy.
- * Mechanical energy.

First law

Alo though the energy May be converted from one form its another. It can't be ~~c~~ greated or detroyed.

$\Delta E = q - w$

ΔE - Internal energy change

q - Heat observed the System

w - Work done of the System

Other State 1st law

The energy May Change from one to another, the total amount of it in an Isolated System always remains unchanged

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Internal Energy :-

i) Every Substance is associated with a certain amount of Energy is known as internal energy.

ii) It is denoted by E.

iii) Internal energy of a Substance is due to its Molecular Consitution and the Motion of the Molecules.

iv) The contributed of the states Factors are internal potentional energy. and Internal kinetic Energy.

Intenal Energy = Internal patential Energy + Internal kinetic Energy

v) Internal energy of a System where is varies with the temperture, volume, pressure, chemical composition

vi) The absalute Value of the Internal energy of the System can't be determain.

vii) But, the change in of the Internal energy of the System (ΔE)

viii) It can be Measured (changes in Pressure, temperature, Volume)

$\Delta E = E_2 - E_1$

$E_1 \cdot E_2$ = Internal Energy of a System intial and Final States

ΔE - Change in Internal Energy.

Internal Energy changes of the System depends upon the intial and Final State of the System.

It is indepentend of path.

Enthalpy [H]

In chemistry generally the operations and carried out in open Vessels at constant pressur.

$\Delta E = Q - P$

According to 1st law.

$\Delta E = Q - W$

$\Delta E = Q - P\Delta V$

$E_2 - E_1 = Q - P\Delta V \quad \therefore \Delta V = V_2 - V_1$

$= Q - P(V_2 - V_1)$

$= Q - PV_2 + PV_1$

$Q = E_2 - E_1 + PV_2 - PV_1$

$$Q = (E_2 + pV_2) - (E_1 + pV_1)$$

The Quantity on the right hand side of the above equation are state Function of the System. So New State Fuction is called Enthalpy is defind as follows.

$$H = E + PV$$

$$Q = H_2 - H_1$$

$$Q = H_2 - H$$

$$= \Delta H_p$$

The change in enthalpy at constat pressure (ΔH_p) is equal to Heat observed by a System in a process at Constant pressure.

The Varies with P, V, T and constant depends upon concentration of the Solution.

It is Not possible to determain the absolute value of enthalpy. of the System.

The change in any Variables of the System can be Measured.

Reolation between ΔH & ΔE.

$$\Delta H = \Delta E + p\Delta V$$

at constant pressure.

$$dH = dE + pdv.$$

$$\Delta H = Q - pdv$$

$$\Delta V = 0 \text{ (constant Volume)}$$

$$\Delta E_V = QV$$

Malar Heat capacity of a gas : at constant pressure : C_p

Consider enthalpy of the System as a function of pressure and temperature For a small change in the System . change in enthalpy is given by the Complete differential equation

$$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_P dT$$

In a Constant pressure process, $dp = 0$

$$\therefore dH = \left(\frac{\partial H}{\partial T}\right)_P dT \text{ — } ①$$

and

Heat capacity

$$dH = q_p \; ; \; q_p = \left(\frac{\partial H}{\partial T}\right)_P dT$$

$$\frac{q_p}{dT} = \left(\frac{\partial H}{\partial T}\right)_P , \; dT = C_p$$

Cp is the Molar Heat capacity of a gas at constant pressure

Definition:

$$Cp = \frac{qp}{dT}$$

The Molar Heat capacity of a gas at Constant pressure is defined as the amount of Heat required the raise the temperature of one Mole of the gas at constant pressure through on degree

Thermodynamic definition

H - enthalpy

$$Cp = \left(\frac{\partial H}{dT}\right)_P$$

The Molar Heat capacity of a gas at constant pressure is thermodynamically defined as the rate of change of enthalpy with temperature at constant pressure.

Relationship between ΔH and cp

Consider enthalpy of the System as a fue) function of pressure and temperature

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Relationship between ΔH and cp.

Δ - Change

From definition $\left(\frac{dH}{dT}\right)_P = Cp$ — ③

At Constant pressure $dH = Cp\,dT$

This is For a Small change

For a Finite change $\Delta H = Cp\,(T_2 - T_1)$ – ④

Molar Heat capacity of a gas at Constant Volume. Cv

Consider internal energy of a System as a Function of Volume and temperature

$$E = f(V,T)$$

When there is a change in state of System, Internal energy change is given by the following complete differential equation

$$dE = \left(\frac{dE}{dV}\right)_T dV + \left(\frac{dE}{dT}\right)_V dT. \quad — ⑤$$

According of first laws

$$dE = q - w$$

$$q - w = dE \quad — ⑥$$

Substituting ⑥ in ⑤

$$q - w = \left(\frac{dE}{dV}\right)_T dV + \left(\frac{dE}{dT}\right)_V dT$$

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At constant Volume $dv = 0$, $W = 0$

$$\therefore q_v = \left(\frac{dE}{dT}\right)_v dT$$

$$\frac{q_v}{dT} = \left(\frac{dE}{dT}\right)_v = C_v \quad — ⑦$$

Here C_v is the Molar heat Capacity of a gas at Constant Volume.

Definition

$$C_v = \frac{q_v}{dT}.$$

The Molar Heat Capacity of a gas at constant Volume is defined as Heat required to raise the temperature at constant Volume

Relationship between ΔE and C_v

From definition $\left(\frac{dv}{dT}\right)_v = C_v$

$\therefore$ At constant Volume $dE = C_v dT$. — ⑧

This is for a Small change. For a Finite change

$$\Delta E = C_v (T_2 - T_1). \quad — ⑨$$

RelationShip between Cp and Cv

Molar Heat capacity of a gas depends upon pressure and temperature. Molar Heat capacity at constant pressure is denoted at cp and at constant Volume as Cv. The relation between cp and cv is obtained as follows

$$E = f(v,T)$$

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dv$$

$$dE = C_v dT + \left(\frac{\partial E}{\partial V}\right)_T dv \quad \text{—⑩}$$

According to first law $dE = q - P_{op} dv$

$$q = dE + P_{op} dv \quad \text{—⑪}$$

substituting ⑩ in ⑪

$$q = C_v dT \left(\frac{\partial E}{dv}\right)_T dv + P_{op} dv \quad \text{—⑫}$$

If $P_{op} = P$ for constant pressure process

$$q_p = C_v (\partial T)_P + \left(\frac{\partial E}{\partial V}\right)_T (\partial v)_P + P(\partial v)_P$$

dividing by $(\partial T)_P$

$$\left(\frac{q}{\partial T}\right)_P = C_v + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

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$$C_P = C_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P - C_V = \left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] \left[\frac{\partial V}{\partial T}\right)_P \quad - ⑫$$

This is a general Expression. For an ideal gas

$$\left(\frac{\partial E}{\partial V}\right)_T = 0 \quad - ⑬$$

and

$$PV = RT$$

$$\frac{V}{T} = \frac{R}{P} \quad - ⑭$$

differentiating at constant P

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

Substituting ⑬ and ⑭ in ⑫

$$C_P - C_V = R$$

This is the relation between Cp and Cv.

The difference between Cp and Cv is equal to the gas Constant.

Calculation of W, Q, dE (dU) and dH for the Expansion of ideal and real gases - Under isothermal and adiabatic conditions for reversible process.

Work done during isothermal changes for ideal gases.

According to First law of Thermodynamics

$$\Delta E = Q - W$$

For an isothermal process $\Delta E = 0$

$$\therefore \quad Q = W$$

i.e, For an isothermal process

Heat absorbed = Work done

The magnitude of W or Q depends on the Manner in which the process is Carried out. i.e, whether it is called out reversibly or irreversibly

Work done during isothermal reversible (process) Expansion of an ideal gas.

Expressions : $W = 2.303\ nRT \log \frac{V_2}{V_1}$

or

$$W = 2.303\ nRT \log \frac{P_1}{P_2}$$

For one mole of an ideal gas

$$w = 2.303\, RT \log \frac{V_2}{V_1}$$

or

$$w = 2.303\, RT \log \frac{P_1}{P_2}$$

Derivation

When the isothermal Expansion is carried out reversibly work done can be obtained as follows

$$w = P_{op}\, dv$$

For reversible Expansion

$$P_{op} = P$$

$$w = Pdv$$

If n mole of ideal gas is taken P is $\frac{nRT}{V}$

Substituting the Value of P

$$w = \frac{nRT}{V}\, dv$$

Integration of the equation gives the def definite quantity of work done in a reversible isothermal Expansion of an ideal gas

$$w = nRT \int_{V_1}^{V_2} \frac{dv}{V} = nRT \ln \frac{V_2}{V_1}$$

$$w = 2.303\, nRT \log \frac{V_2}{V_1}$$

Replacing V with $\frac{RT}{P}$ we get the following Expression of the work done in a reversible isothermal Expansion of an ideal gas

$$W = 2.303\, nRT \log \frac{P_1}{P_2}$$

Workdone during adiabatic changes for ideal gases

Since in an adiabatic process no Heat is absorbed or evolved $Q = 0$

From first law of thermodynamics

$$\Delta E = Q - W$$

$$Q = 0$$

$$\Delta E = -W$$

$$W = -\Delta E$$

$$\Delta E = C_V \Delta T$$

$$W = -\Delta E = -C_V \Delta T$$

From the above equations, it is clear that in an adiabatic change, ΔE, ΔH and W depends on the Magnitude of ΔT. ΔT depends on the Final Temperature of the Process. Final temperature depends on the Manner is which the Process is Carried Out. i.e whether it is Carried out reversibly or irreversibly. Thus the Magnitude of ΔE, ΔH and W Vary with the nature of the process.

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Workdone during adiabatic reversible Expansion of an ideal gas

First law

$$dE = q - w$$

$$q = dE + W$$

$$E = f(T, V)$$

$$dE = \left(\frac{dE}{dT}\right)_V dT + \left(\frac{dE}{dV}\right)_T dV$$

$$q = \left(\frac{dE}{dT}\right)_V dT + \left(\frac{dE}{dV}\right)_T dV$$

$$\boxed{W = pdV}$$

$$q = \left(\frac{dE}{dT}\right)_V dT + \left(\frac{dE}{dV}\right)_V dV + pdV \text{ — ①}$$

Adiabatic Changes $q = 0$

ideal gas $\left(\frac{dE}{dV}\right)_T = 0$

$$\left(\frac{dE}{dT}\right)_V = C_V$$

Sub ①

$$0 = C_V dT + 0 + pdV$$

$$pdV = -C_V dT$$

Workdone in an adiabatic Expansion pdV

i.e

$$w = \int pdV$$

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$$= -\int_{T_1}^{T_2} cv \, dT$$

$$= -cv \left[T\right]_{T_1}^{T_2}$$

$$= -cv \left[T_2 - T_1\right]$$

$$W = cv \left[T_1 - T_2\right]$$

Difference between Reversable and irreversable workdone Expansion of ideal gas.

Reversible	Irreversable
i) Work obtainable will be maximum	i) Will not be maximum
ii) It proceeds Very slow	ii) It proceeds in a measurable rate

Difference between Isothermal and adiabatic process.

property	Isothermal process	adiabatic process.
Temperature	Constant	changes.
Heat change	$q = w$, Varies with the Nature of process	$q = 0$, Varies with the nature of the process.
ΔE	$\Delta E = 0$, Doesn't Varies with the Nature of the process	$\Delta E = -w$, i.e $= C_V \Delta T$ Varies with the Nature of the process

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ΔH	$\Delta H = 0$. Does not Varios with the Nature of the Process	$\Delta H = C_p \Delta T$ Varies with the Nature of the proc
Final pressure	More	less
Final Volume	More	less
Workdone	More	less

Workdone during isothermal and Adiabatic changes for a Real gas.

We know that only ideal gases obey the equation of a state $PV = nRT$ Real gas do not obey this equation at High Pressure and low temperature. For real gases, we use vanderwaals equation viz.

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

In this equation the term an^2/V^2 is called the internal pressure term this accounts for the attractive forces between molecules.

Workdone in isothermal changes for a real gas:

We know Work done W is given by

$$W = \int p\,dv$$

from Vander Waal's equation

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

i.e

$$P + \frac{an^2}{V^2} = \frac{nRT}{(V-nb)}$$

or

$$P = \frac{nRT}{V-nb} - \frac{an^2}{V^2}$$

Multiplying by dv

$$Pdv = \left(\frac{nRT}{V-nb}\,dv\right) - \frac{an^2}{V^2}\,dv$$

i.e

$$W = \int p\,dv$$

$$= \int_{V_1}^{V_2} \frac{nRT}{V-nb}\,dv - an^2 \int_{V_1}^{V_2} \frac{dv}{V^2}$$

$$W = nRT \ln\left(\frac{V_2 - nb}{V_1 - nb}\right) + an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

The above Expression given the work done in isothermal changes for real gases.

Workdone in adiabatic changes for a real gas :-

In an Adiabatic changes the System is thermally insulated So $Q = 0$ and Hence $\Delta E = -W$

we know,

$$dE = \left(\frac{dE}{dT}\right)_V dT + \left(\frac{dE}{dv}\right)_T dv$$

Substituting

$$\left(\frac{dE}{dT}\right)_V = nC_V$$

and

$$\left(\frac{dE}{dT}\right)_V = \frac{an^2}{V^2}$$

In the above Equation

$$dE = nC_V\, dT + \frac{an^2}{V^2} dv$$

$$\int_{E_1}^{E_2} dE = nC_V \int_{T_1}^{T_2} dT + an^2 \int_{V_1}^{V_2} \frac{dv}{V^2}$$

$$E_2 - E_1 = \Delta E = nC_V (T_2 - T_1) - an^2\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$$

$$w = -\Delta E = -nC_V (T_2 - T_1) + an^2\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$$

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The above Expression gives the work done in Adiabatic changes for real gases.

Joule's law:

The energy of the gas is a function of temperature only, it is independent of Volume. ~~th~~

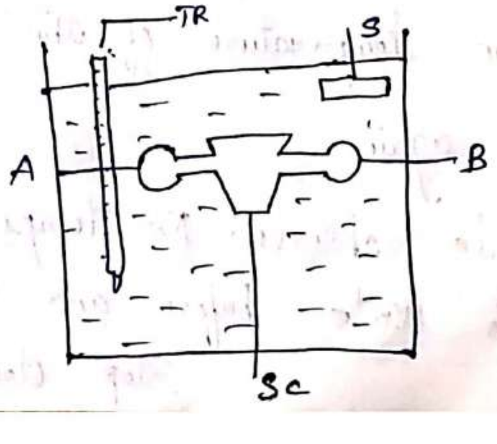
The law may be represented mathametically as $\left(\frac{dE}{dV}\right)_T = 0$

Measurment of $\left(\frac{dE}{dV}\right)_T$ (or) Joule's Experiment:

The Determination of $\left(\frac{dE}{dV}\right)_T$ with readily measurable Quantities is not easy.

For gases it can be measured. in the principle of Experiment by Joule.

The Apparatus used for the purpose of Measurment.



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Two Containers A and B Connected through a Stop clock.

A is filled with a gas. At a Pressure. B. While B is evacuted (empty)

The Apparatus is immersed in large water tup and is allowed to equlibrate with water at the temperature T

Which is read on the thermo meter TR.

The water is stirred. Vigorously (fastly)

After the water equlibrium attained. The Stop clock is opened and the gas expands to fill the containers A and B Uniformly.

The System is allowed to thermal come to thermal equlibrium with the water tup.

The temperature of the water is read again.

Joule observed No temperature difference in water before and after opening Stop clock.

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Interpretation of the Experiment

The gas in ~~A~~ container A Expends against o(zero) opposing Pressure. So No work is produced $w=0$

This called free Expansion of of gas.

According to the First law

$$dE = q - w$$

$$dE = q - 0$$

$$dE = q$$

we know that.

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV$$

$$dV = 0 \quad ; \quad dV \neq 0$$

$$dE = \left(\frac{\partial E}{\partial T}\right)_V \quad ; \quad dE = \left(\frac{\partial E}{\partial V}\right)_T$$

limitation.

* The Joule Thomson Experiment is not Correct real gas

* The Joule's apparatus the large Heat capacity at the dup.

* The ideal gas obey Joule's law

Temperature dependence of ΔH - Kirchoff's equation thermodynamic derivation :

Heat of reaction at constant pressure can be Expressed is terms of molar enthalpies of reactants and products.

$$\Delta H_P = H_P - H_R$$

Differentiating this equation with resped to temperature

$$\frac{d\Delta H_P}{dT} = \frac{dH_P}{dT} - \frac{dH_R}{dT} \quad — ①$$

we know that,

$$\frac{dH_P}{dT} = (C_P)_P$$

$$\frac{dH_R}{dT} = (C_P)_R$$

Substituting these above Values in ①

$$\frac{d\Delta H}{dT} = (C_P)_P - (C_P)_R$$

$$\frac{d\Delta H}{dT} = \Delta C_P$$

equation 2 is the Mathematical Expression of Kirchhoff's equation, Rearrangement kirchhoff's equation

$$d\Delta H = \Delta cp\,dT$$

Ed Integrating between two temperature

$$\int_{H_1}^{H_2} d\Delta H = \int_{T_1}^{T_2} \Delta cp\,dT$$

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta cp\,dT$$

For a small temperature difference. Δcp may be taken as a constant

$$\therefore \Delta H_2 = \Delta H_1 = \Delta cp\,(T_2 - T_1)$$

$$\Delta H_2 = \Delta H_1 + \Delta cp\,(T_2 - T_1) \quad - ③$$

Equation 3 is the intergrated form of Kirchhoff's equation. This is another mathematical Expression of Kirchhoff's equation

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unit - III

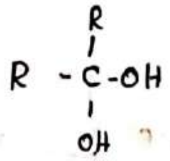
chemistry of alcohols, phenals, and Ether.

Alcohols:

compounds which contains hydroxyl group as a fuctions. groups. (R-OH)
↓
(alkyl, aryl)

CH_3OH, CH_3CH_2OH, $CH_3CH_2CH_2OH$.
methanol, ethanol n- proponol.

Alcohols —
- monohydric (R-OH)
- Dihydric
- polyhydric



$R-\overset{R}{\underset{OH}{C}}-OH$

Dihydric pol

CH_2OH
|
CH_2OH
(Glycol)

Nomeculature of alcohals.

Select the largest carbon chain containing hydroxyl group

Give Number to the compound carring OH - group lowest passiable Numbers.

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Change the corresponding alkane into alcohol. eg: Methane |-e +ol.

Give the Numbers for position of Hydroxyl group.

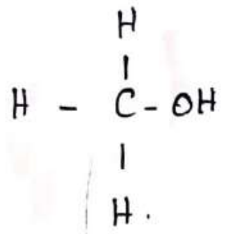
Give Numbering for other Substituents

$CH_3CHCl\ CH_2CH_2OH$.

3 - chloro butanol.

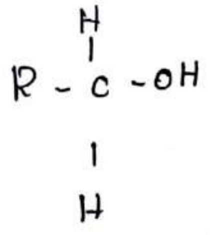
Alcohols.

↳ Sources
- → Hydroboration
- → oxymercuration
- → Hydration of alkenes.



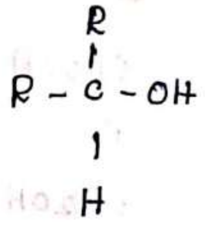
$$H-\overset{H}{\underset{H}{C}}-OH$$

Methano.



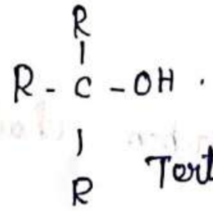
$$R-\overset{H}{\underset{H}{C}}-OH$$

Primary



$$R-\overset{R}{\underset{H}{C}}-OH$$

Secondary.



$$R-\overset{R}{\underset{R}{C}}-OH$$

Tertiary.

Preparations

(1) Alkaline Hydrolysis (RX)

$$Rx + NaOH \xrightarrow{H_2O} ROH + NaX$$

$$CH_3Cl + NaOH \xrightarrow{H_2O} CH_3OH + NaCl.$$

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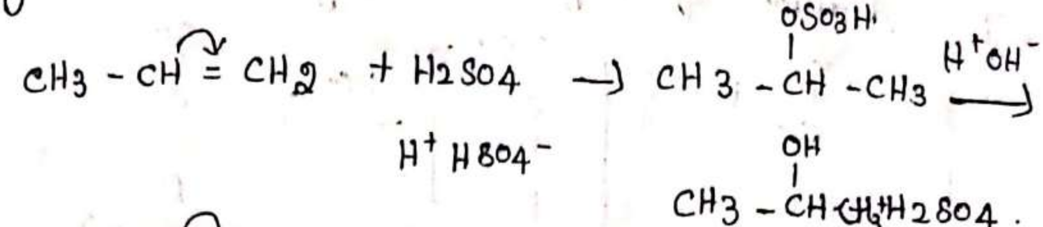
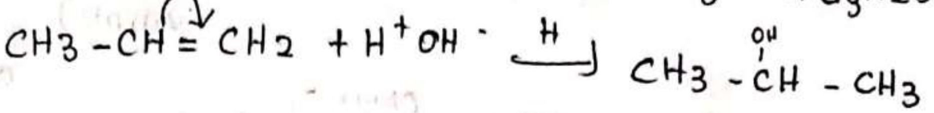
2. Hydraction of alkenes :-



$$CH_3 - CH = CH_2 + \underset{H^+ HSO_4^-}{H_2SO_4} \rightarrow CH_3 - \overset{OSO_3H}{CH} - CH_3 \xrightarrow{H^+OH^-} CH_3 - \overset{OH}{CH} ~~CH_3~~ H_2SO_4 .$$



$$CH_3 - CH = CH_2 + H^+OH^- \xrightarrow{H} CH_3 - \overset{OH}{CH} - CH_3$$

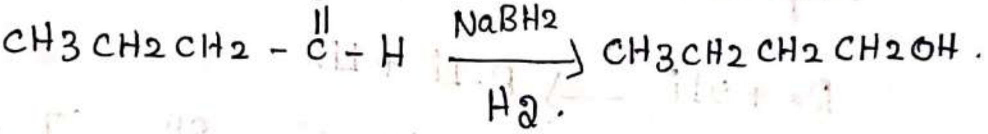
③. Hydroboration

$$CH_3 - CH = CH_2 \xrightarrow[H_2O / OH^-]{B_2H_6 \text{ (Diborane)}} CH_3CH_2CH_2OH$$

4. Hydrolysis of ester.

$$R - \overset{O}{\overset{\|}{C}} - O - R + HOH \rightarrow R ~~COHR~~ + R - \overset{O}{\overset{\|}{C}} - OH .$$

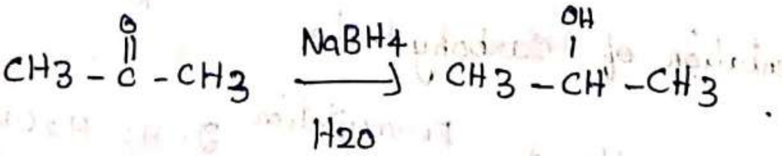
5. catalytic hydrogenataion of aldehydes.



$$CH_3CH_2CH_2 - \overset{O}{\overset{\|}{C}} - H \xrightarrow[H_2]{NaBH_2} CH_3CH_2CH_2CH_2OH .$$

6. Reduction of aldehydes and ketons with metal hydrides.

$$CH_3CH_2CH_2 - \overset{O}{\overset{\|}{C}} - H \xrightarrow[H_2O]{LiAlH_4} \underset{n\text{-Butanol}}{CH_3CH_2CH_2CH_2OH} .$$



$$CH_3 - \overset{O}{\overset{\|}{C}} - CH_3 \xrightarrow[H_2O]{NaBH_4} CH_3 - \overset{OH}{CH} - CH_3 .$$

7. Hydrolysis of acid halides and anhydrides.

$$R - \overset{O}{\overset{\|}{C}} - Cl + HOH \rightarrow R - \overset{O}{\overset{\|}{C}} - OH + HCl .$$

$$R - \overset{O}{\overset{\|}{C}} - O - \overset{O}{\overset{\|}{C}} - R + HOH \rightarrow R - \overset{O}{\overset{\|}{C}} - OH + R - \overset{O}{\overset{\|}{C}} - OH$$

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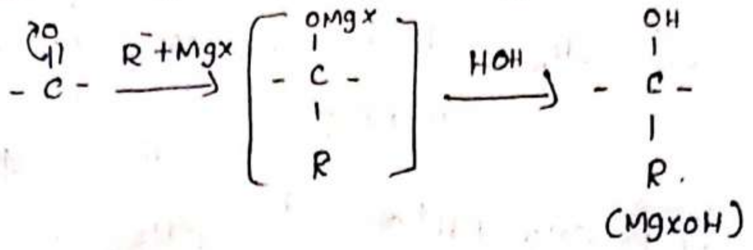
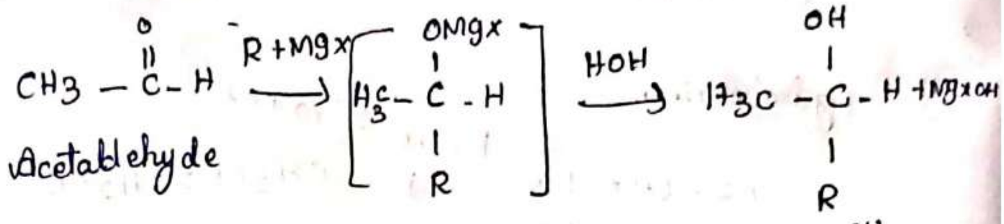
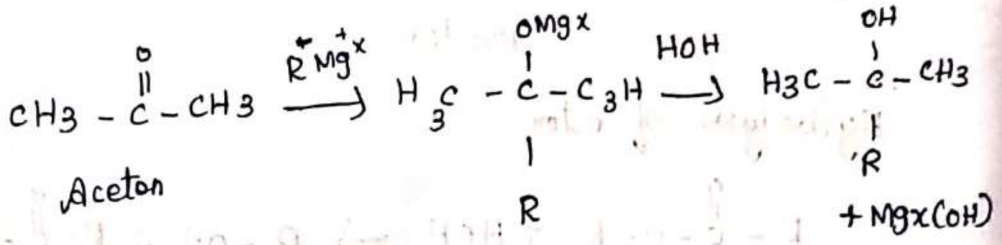
7. Addition of Rmgx to Carbonyl compounds ;



$$-\overset{O}{\overset{\|}{C}}- \xrightarrow{R^- + Mgx} \left[-\underset{R}{\overset{OMgx}{C}}- \right] \xrightarrow{HOH} -\underset{R}{\overset{OH}{C}}- \quad (Mgx OH)$$



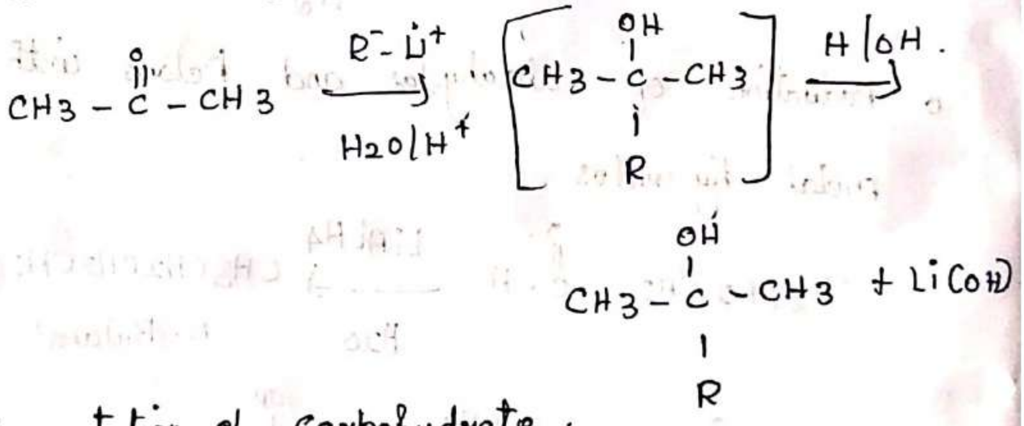
$$\underset{\text{Acetaldehyde}}{CH_3-\overset{O}{\overset{\|}{C}}-H} \xrightarrow{R^- + Mgx} \left[H_3C-\underset{R}{\overset{OMgx}{C}}-H \right] \xrightarrow{HOH} H_3C-\underset{R}{\overset{OH}{C}}-H + MgxOH$$



$$\underset{\text{Aceton}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} \xrightarrow{R^- Mg^+ x} H_3C-\underset{R}{\overset{OMgx}{C}}-C_3H \xrightarrow{HOH} H_3C-\underset{R}{\overset{OH}{C}}-CH_3 + Mgx(OH)$$

8. Reaction of Lithium compounds with Carbonyl compounds

$Rx + 2Li \longrightarrow R-Li + Lix$

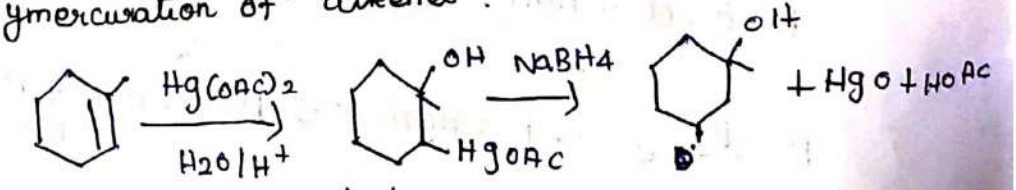


$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[H_2O/H^+]{R^- - Li^+} \left[CH_3-\underset{R}{\overset{OH}{C}}-CH_3 \right] \xrightarrow{H/OH} CH_3-\underset{R}{\overset{OH}{C}}-CH_3 + Li(OH)$$

9. Fermentation of Carbohydrate .

$\underset{\text{Glucose}}{C_6H_{12}O_6}$ + Yeast $\xrightarrow{\text{Fermentation}}$ $2CH_3CH_2OH + 2CO_2\uparrow$

10. oxymercuration of alkenes :



Acetoxy mercuration

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Physical properties :-

* lower alcohols are clourless foxic liquids .

* They have characteristics Smell

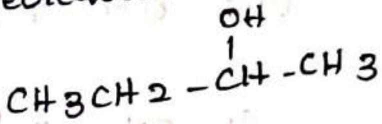
* Bolling point increases with increasing Molecular wight .

* Among insomeric alcohol branching increases Bolling point decreases .

$CH_3CH_2CH_2CH_2OH$

1- butanol 1°

B.P - 118°c

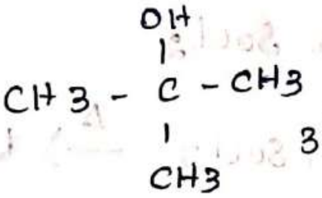


$CH_3CH_2-CH(OH)-CH_3$

2 - butanol

98°c

2°



$CH_3-C(OH)(CH_3)-CH_3$

3°

* Bolling point of alcohols are Higher than the corresponding albanes. due to the Hydrogen bonding

* lower alcohols are soluble in water . As, we go Higher alcahols are not soluble in water .

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Chemical properties:-

1. Reaction with Active Metals (Na (or) K)

$$2R-OH + 2Na \xrightarrow{\Delta} 2R-O^{-}Na^{+} + H_2\uparrow$$

$$2CH_3-OH + 2Na \xrightarrow{\Delta} 2CH_3-O^{-}Na^{+} + H_2\uparrow$$

2. Ad Reaction with PX_5 and PX_3.

$$R-OH + PX_5 \xrightarrow{\Delta} R-X + HX + POX_3$$

$$CH_3-OH + PX_5 \xrightarrow{\Delta} CH_3-X + HX + POX_3$$

$$3R-OH + PX_3 \xrightarrow{\Delta} 3R-X + H_3PO_3$$

$$3CH_3-OH + PCl_3 \xrightarrow{\Delta} 3CH_3-Cl_3 + H_3PO_3$$

3. Reaction with $SOCl_2$.

$$R-OH + SOCl_2 \xrightarrow{\Delta} R-Cl + HCl + SO_2\uparrow$$

$$CH_3-OH + SOCl_2 \xrightarrow{\Delta} CH_3Cl + HCl + SO_2\uparrow$$

4. Reaction with HX.

$$R-OH + HX \longrightarrow R-X + H_2O$$

$$CH_3CH_2-OH + HCl \longrightarrow CH_3CH_2Cl + H_2O.$$

5. Reaction with HNO_3.

$$R-OH + HNO_3 \longrightarrow R-NO_3 + H_2O$$

$$CH_3-OH + HNO_3 \longrightarrow CH_3-NO_3 + H_2O.$$

Alkylhalides.

6. Reaction with H_2SO_4.

$$R-OH + H_2SO_4 \xrightarrow{\text{Room Temp.}} R-OSO_3H + H_2O$$

Alkylhydrogen Sulphate

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$CH_3CH_2OH \xrightarrow[170^\circ C \quad -H_2O]{Con.H_2SO_4} CH_2=CH_2 + H_2O$

7. Dehydration of alcohols to ethers.

$CH_3CH_2\boxed{OH + H}OCH_2CH_3 \xrightarrow[140^\circ C]{Con.H_2SO_4} CH_3CH_2-O-CH_2-CH_3 + H_2O.$

8. Reaction with acid chloride and Anhydride.

$R-OH + CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-OR + HCl.$

ester.

$CH_3-OH + CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3 + HCl.$

0

$R-OH + CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-OH + CH_3-\overset{O}{\overset{\|}{C}}-O-R.$

$CH_3CH_2OH + CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-OH + CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3CH_2$

9. Reaction with carboxylic acids.

$R-\overset{O}{\overset{\|}{C}}-O-CH_3 + H_2O$

$R-OH + CH_3COOH \longrightarrow R-\overset{\|}{C}H_3CO_2 + H_2O$

10 Reaction with grignard reagents.

$R'-OH + \cancel{R}Mg\cancel{X} \longrightarrow \cancel{R-OH} + RMgX.$

$R-OH + RMgx \xrightarrow{\Delta} R-O^-Mg^+x + RH.$

11. Reduction

$R-OH + 2HI \longrightarrow R-H + H_2O + I_2.$

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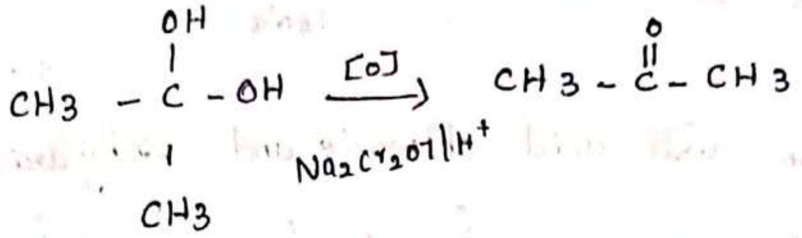
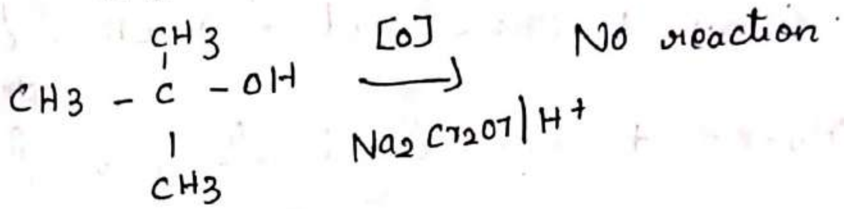
12\. oxidation :

$$CH_3-CH_2OH \xrightarrow[Na_2Cr_2O_7|H^+]{[O]} CH_3CHO \xrightarrow[Na_2Cr_2O_7|H^+]{[O]} CH_3COOH$$



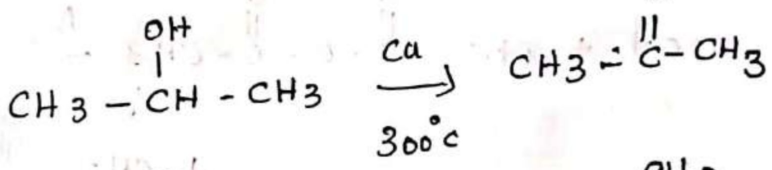
$$CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH \xrightarrow[Na_2Cr_2O_7|H^+]{[O]} CH_3-\overset{\overset{O}{||}}{C}-CH_3$$



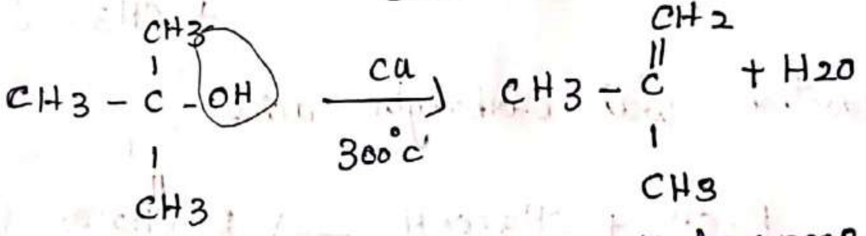
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH \xrightarrow[Na_2Cr_2O_7|H^+]{[O]} \text{No reaction}$$

13\. Reaction with hot Cu

$$CH_3CH_2OH \xrightarrow[300°c]{Cu} CH_3CHO$$



$$CH_3-\overset{\overset{OH}{|}}{CH}-CH_3 \xrightarrow[300°c]{Cu} CH_3-\overset{\overset{O}{||}}{C}-CH_3$$



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH \xrightarrow[300°c]{Cu} CH_3-\overset{\overset{CH_2}{||}}{\underset{\underset{CH_3}{|}}{C}} + H_2O$$

2-Methyl propene.

Distinction of 1°, 2°, 3° alcohols

1) with lucas test [HCl + $ZnCl_2$]

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

3° alcohols reacts faster with lucas reagent cloudiness appears immediately.

2° alcohols reacts slower than 3° alcohols with lucas reagent cloudiness appears after 5 min

1° alcohols reacts ~~slower~~ even slower than 2° alcohols at room temperature with lucas reagent. No cloudiness appears.

Uses of alcohols :-

Methanol (used)

1. It is used as a Solvent for paints & Varnishes

It is used as an antifreeze for automobile Radiators

To denature ethyl alcohols

Used for the Manufacture of formaldehyde

Used as a fuel.

Ethanol (uses)

It is used as a Solvents and Varnishes, Industrial Solvent.

It is used as an antifreeze for automobile Radiators.

It is used to prepare alcoholic beverages.

It is used to prepare drugs and perfumes.

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It is Used as an antiseptic in Hospitals

It is used as an preservative for Biological Specimens.

It is Used to prepare acetaldehyde, ethylacetate, acetic acid.

Absolute alcohol (100% alcohol).

It is 100% pure alcohol. is called Absolute alcohol.

100% ethyl alcohol.

<u>Rectified alcohol</u>

95% ethyl alcohol + 5% H_2O.

To prepare absolute alcohol.

lime water ([illegible])

$$\underset{95\%}{CH_3CH_2OH} + \underset{5\%}{H_2O} \xrightarrow{CaO} \underset{100\%}{CH_3CH_2OH} + Ca(OH)_2$$

Denature alcohols:

It is a Commercial ethyl alcohol in which Small amounts of poisonous Substance Have been added to the alcohol.

Methyl al Methanol (or) pyridine

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Diols

Compound which contains two hydoroxyl group are called Diols.

A compounds which contains two hydroxyl group on adjectionent carbon are called Glycols. (1,2, diols)

Ethylene glycol or Ethane diol.

$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}$$

Ethane diol is an example for dihydric alcohols.

preparation

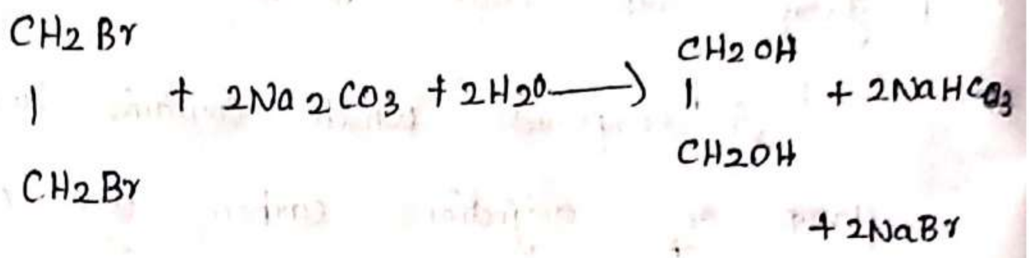
1. Oxcidation of ethylene with dil. KMnO4.

$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + (H_2O + O) \xrightarrow{dil.\ KMnO_4} \begin{array}{l} CH_2OH \\ \| \\ CH_2OH \end{array}$$

2. Oxidiation of ethylene with d OSO4 in the presence of NaHSo3. Sodium Hydrogen Sulphide OS- Osmium (Highest oxidat state)

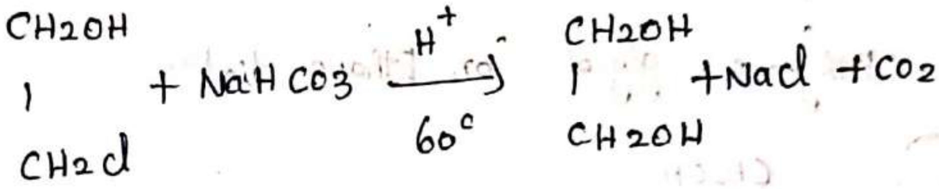
$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + (H_2O + O) \xrightarrow[NaHSO_3]{OsO_4} \begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}$$

3. Hydrolysis of 1,2-diBromo ethane presence Sodium Carbonate :



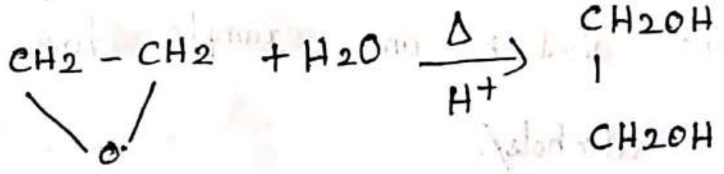
$$\begin{matrix}CH_2Br\\|\\CH_2Br\end{matrix} + 2Na_2CO_3 + 2H_2O \longrightarrow \begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix} + 2NaHCO_3 + 2NaBr$$

4. Reaction of chlorohydrin with NaHCO3



$$\begin{matrix}CH_2OH\\|\\CH_2Cl\end{matrix} + NaHCO_3 \xrightarrow[60^c]{H^+} \begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix} + NaCl + CO_2$$

5. Hydrolysis of ethylene oxide :



$$\underbrace{CH_2 - CH_2}_{O} + H_2O \xrightarrow[H^+]{\Delta} \begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}$$

Physical properties :

* Glycol is a Clourless Viscous liquid

* Glycol has boiling point at 197°c

Melting point - 13°c

* It is Sweet in taste

It observe water easely.

* It is hygroscopic in nature

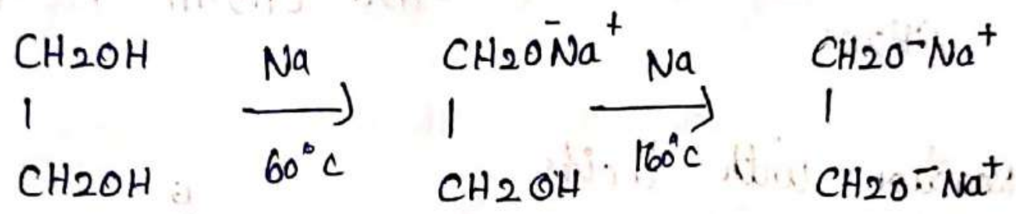
* It is misicible with water and Methanol in all proportions.

* It is insoluble in ether.

chemical properties.

Chemical properties of diol is More Similar like that of Mono hydric alcohols but only one OH -group is reacted at a time

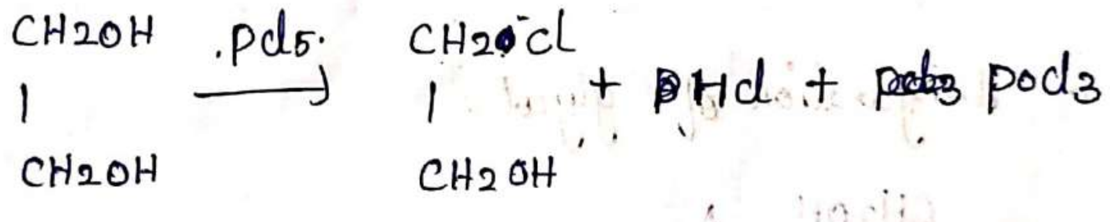
1. Reaction with Na



$$\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array} \xrightarrow[60^\circ C]{Na} \begin{array}{c} CH_2O^-Na^+ \\ | \\ CH_2OH \end{array} \xrightarrow[160^\circ C]{Na} \begin{array}{c} CH_2O^-Na^+ \\ | \\ CH_2O^-Na^+ \end{array}$$

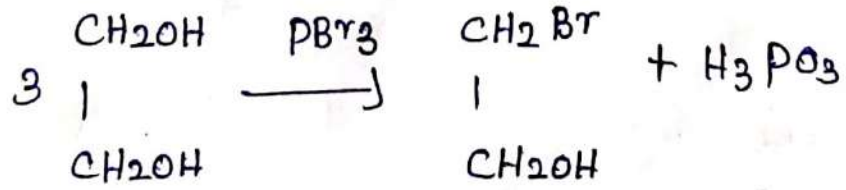
Sodium alkonoxide

2. Reaction with pcl5.



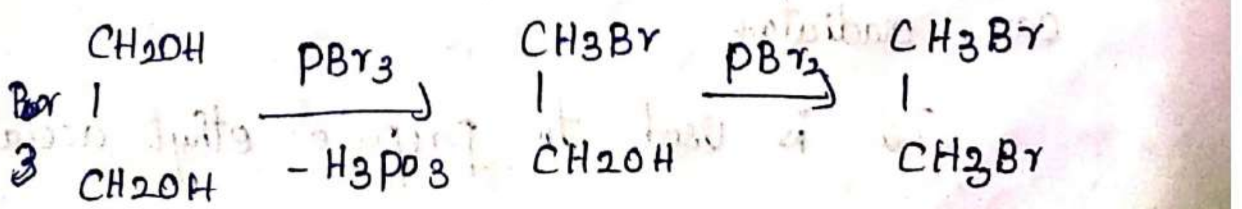
$$\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array} \xrightarrow{pcl_5} \begin{array}{c} CH_2\cancel{O}Cl \\ | \\ CH_2OH \end{array} + \cancel{P}HCl + \cancel{pcl_3}\ POCl_3$$

3. Reaction with PBr3



$$3 \begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array} \xrightarrow{PBr_3} \begin{array}{c} CH_2Br \\ | \\ CH_2OH \end{array} + H_3PO_3$$

(or)



$$\cancel{Bor}\ 3 \begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array} \xrightarrow[-H_3PO_3]{PBr_3} \begin{array}{c} CH_3Br \\ | \\ CH_2OH \end{array} \xrightarrow{PBr_3} \begin{array}{c} CH_3Br \\ | \\ CH_2Br \end{array}$$

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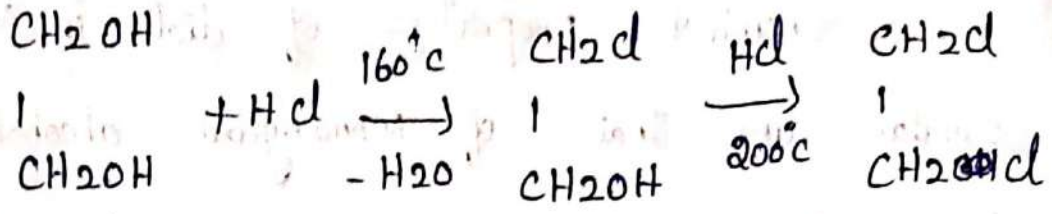
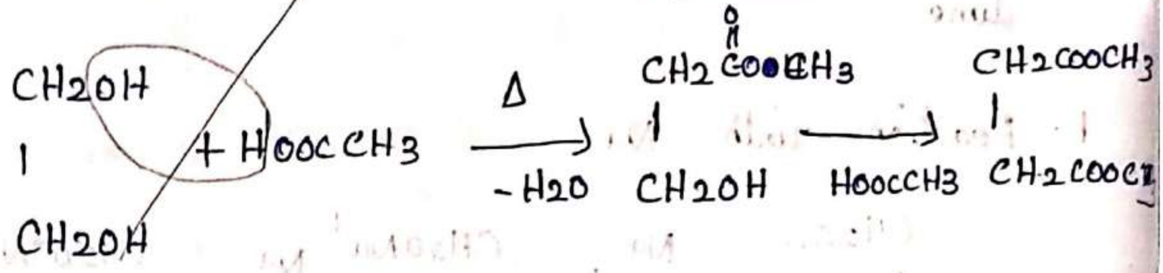
4. Reaction with HCl (HX)



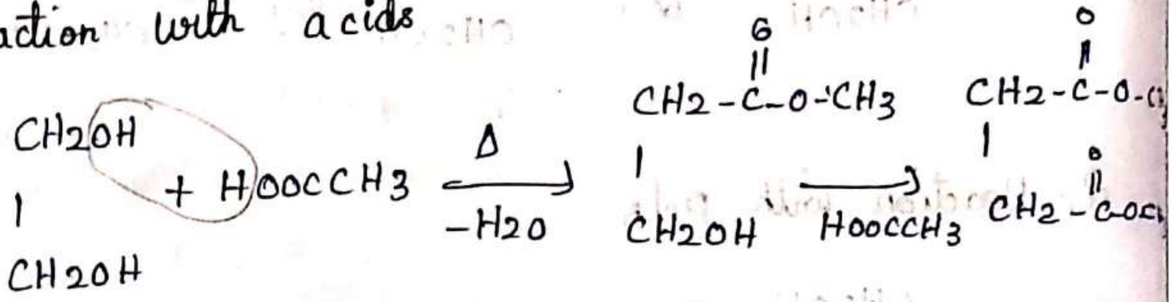
$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + HCl \xrightarrow[-H_2O]{160^\circ C} \begin{array}{l} CH_2Cl \\ | \\ CH_2OH \end{array} \xrightarrow[200^\circ C]{HCl} \begin{array}{l} CH_2Cl \\ | \\ CH_2Cl \end{array}$$

5. Reaction with acids acidic acid <u>weak acid</u>



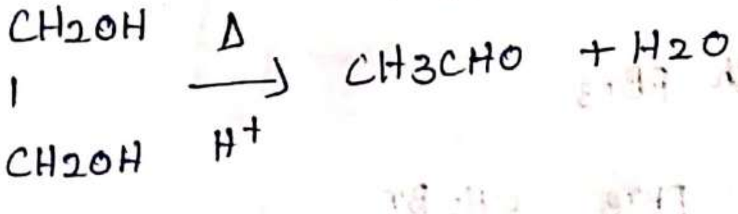
$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + HOOCCH_3 \xrightarrow[-H_2O]{\Delta} \begin{array}{l} CH_2\overset{O}{\overset{\|}{C}}OOCH_3 \\ | \\ CH_2OH \end{array} \xrightarrow[HOOCCH_3]{} \begin{array}{l} CH_2COOCH_3 \\ | \\ CH_2COOCH \end{array}$$

5. Reaction with acids



$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + HOOCCH_3 \xrightarrow[-H_2O]{\Delta} \begin{array}{l} CH_2-\overset{O}{\overset{\|}{C}}-O-CH_3 \\ | \\ CH_2OH \end{array} \xrightarrow[HOOCCH_3]{} \begin{array}{l} CH_2-\overset{O}{\overset{\|}{C}}-O- \\ | \\ CH_2-\overset{O}{\overset{\|}{C}}-OC \end{array}$$

6. Dehydration of glycol.



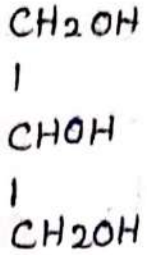
$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} \xrightarrow[H^+]{\Delta} CH_3CHO + H_2O$$

Uses

Glycol is used as an antifreeze for car radiators

It is used to prepare ethyl acetate, ethyl chloride, dichloro ethane and epoxide

Glycerol :- (1,2,3 -propanetriol)



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

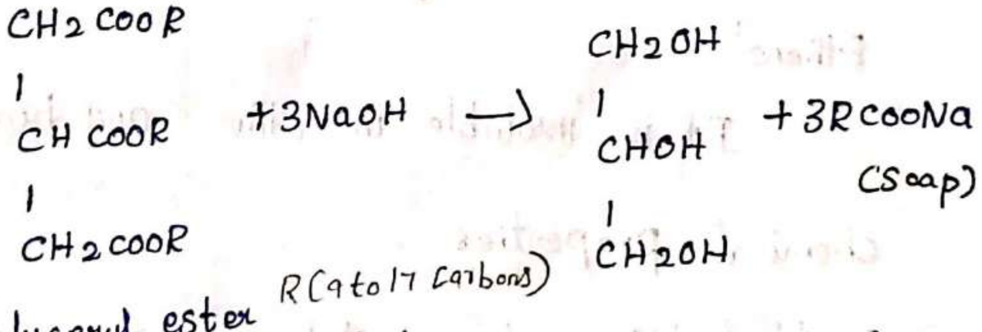
Glycerol is an example for trihydric alcohal

It was formely know as Glycerine

Glycerol is most found in Natural oils and fats as Glyceryl esters of long chain carboxylic acids. (palmitic acid, stereaic acid, oleic acid)

Preparation

i) From Natural oils and fats :-



$$\begin{array}{l} CH_2COOR \\ | \\ CH\,COOR \\ | \\ CH_2COOR \end{array} + 3NaOH \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3RCOONa$$

(Soap)

R(9 to 17 carbons)

Glyceryl ester

Alkaline Hydrolysis of Glyceryl ester gives Glycerol.

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2. From propene

$$CH_3-CH=CH_2+Cl_2 \xrightarrow[-HCl]{600^{\circ}c} CH_2CH=CH_2Cl$$

allylchloride

$$\xrightarrow[-NaCl]{NaOH} OHCH_2CH=CH_2 \xrightarrow[(Hypochloride)]{HOCl} OHCH_2-\overset{OH}{\overset{|}{C}H}-CH_2Cl$$

Allyl alcohol.

$$\xrightarrow{NaOH} \begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + NaCl.$$

Properties

Physical properties

Glyceral is a Colourless odourless and Sweet tastering Syrupy liquid

It has Melting at 29°C

It is readily Soluble in Ester and Ethanol.

It is insoluble in ether and benzene.

Chemical properties:.

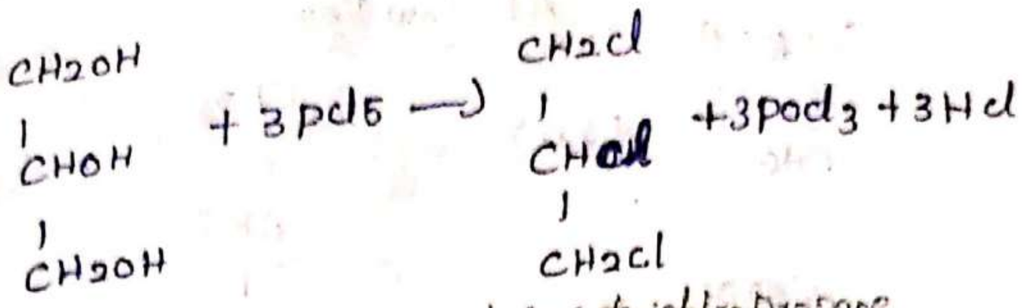
i) Reaction with active Metals.

$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow[low\ T]{Na} \begin{array}{c} CH_2ONa \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow[High\ T]{Na} \begin{array}{c} CH_2ONa \\ | \\ CHOH \\ | \\ CH_2ONa \end{array}$$

Mono Sodium Glycerolate

dy sodium Glycerloate

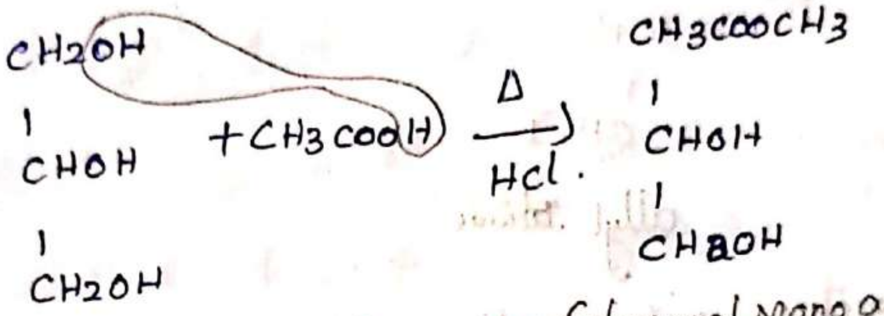
2. Reaction with pcl5.



$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3pcl_5 \longrightarrow \begin{array}{c} CH_2cl \\ | \\ CHcl \\ | \\ CH_2cl \end{array} + 3pocl_3 + 3Hcl$$

1,2,3-trichlro propane

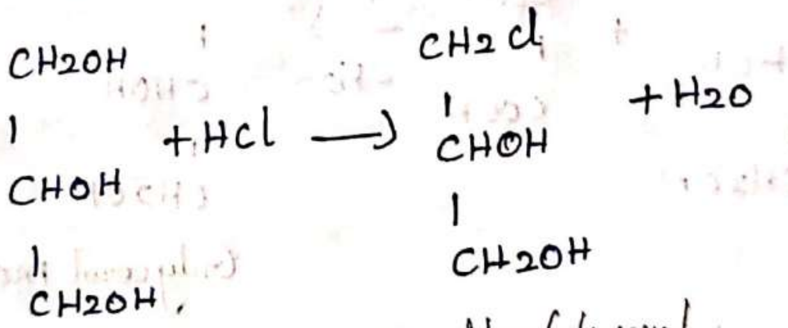
3. Reaction with carboxylic acids.



$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + CH_3COOH \xrightarrow[Hcl.]{\Delta} \begin{array}{c} CH_3COOCH_3 \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Glycerol Mono acetate

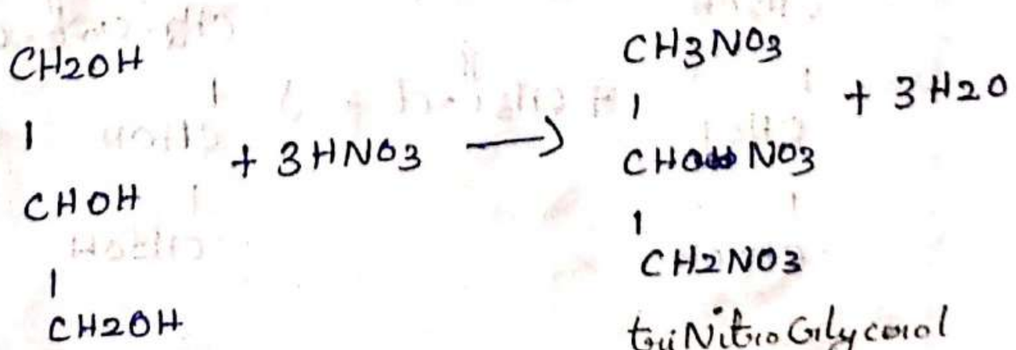
4. Reaction with Hcl.



$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + HCl \longrightarrow \begin{array}{c} CH_2cl \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + H_2O$$

1, chlro Glycerol

5. Reaction with Nitric acid.



$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3HNO_3 \longrightarrow \begin{array}{c} CH_3NO_3 \\ | \\ CHNO_3 \\ | \\ CH_2NO_3 \end{array} + 3H_2O$$

triNitro Glycerol

Explosive - வெடிமருந்து.

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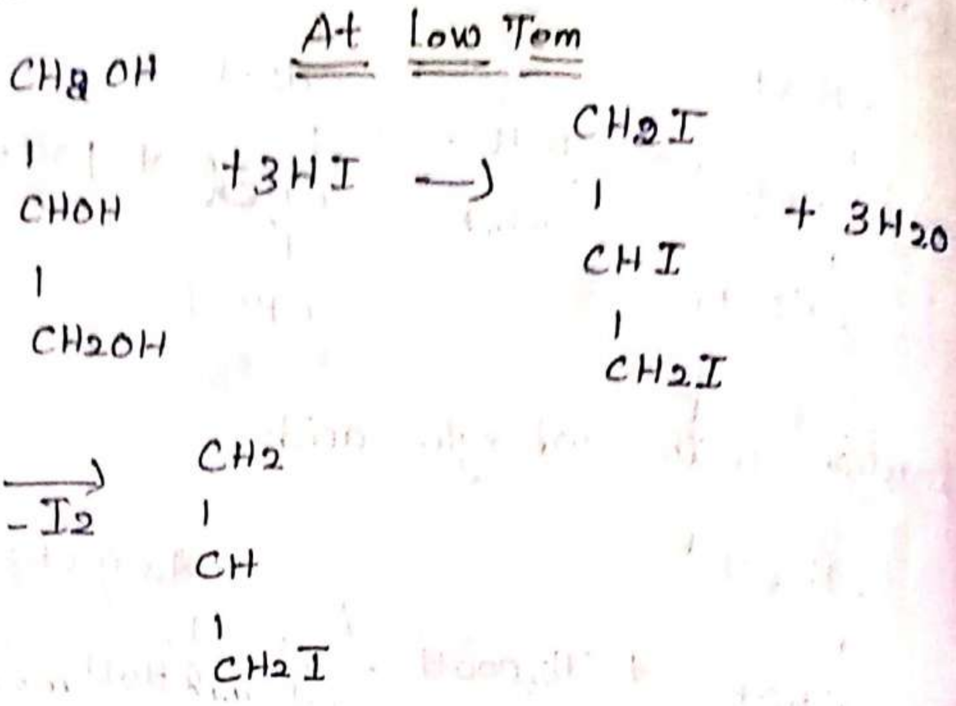
6 Reaction with HI

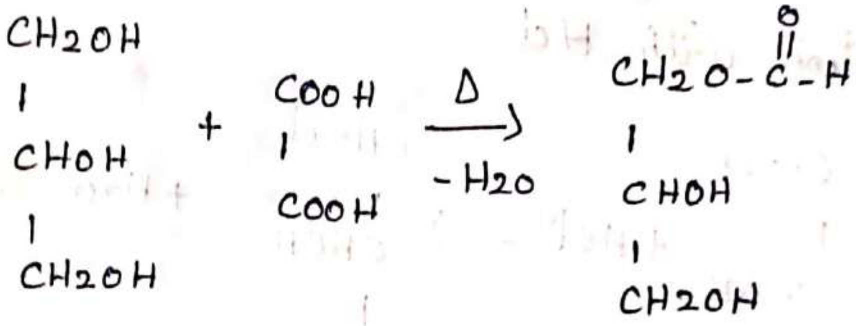


$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3HI \xrightarrow{\text{At Low Tem}} \begin{array}{c} CH_2I \\ | \\ CHI \\ | \\ CH_2I \end{array} + 3H_2O$$

$$\xrightarrow[-I_2]{} \begin{array}{c} CH_2 \\ | \\ CH \\ | \\ CH_2I \end{array}$$

allyl Idiade

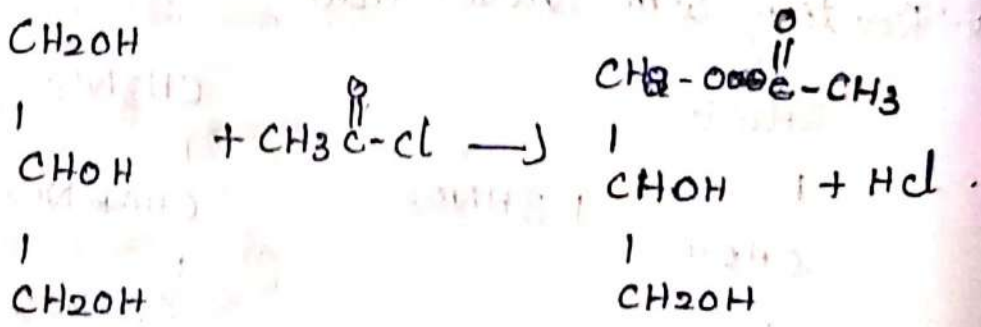
7. Reaction with oxalic acid.



$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \begin{array}{c} COOH \\ | \\ COOH \end{array} \xrightarrow[-H_2O]{\Delta} \begin{array}{l} CH_2O-\overset{O}{\overset{\|}{C}}-H \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Glycerol monoformate

8. Reaction with acetyl choloredo.



$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + CH_3\overset{O}{\overset{\|}{C}}-Cl \longrightarrow \begin{array}{l} CH_2-O\overset{O}{\overset{\|}{C}}-CH_3 \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + HCl.$$

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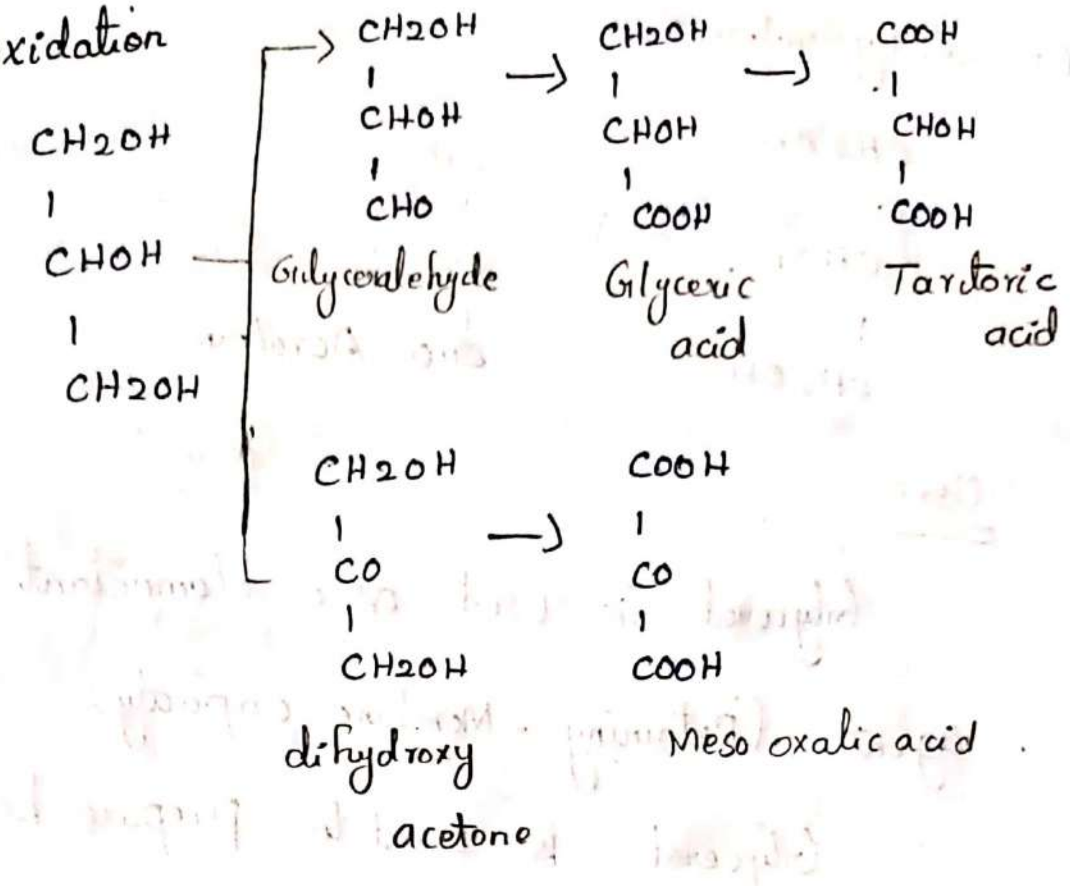
9. oxidation



Glycerol on oxidation with dil. HNO_3 to from a Glyceric acid and Tartoric acid.

Glycerol on oxidation with con. HNO_3 to from a Glyceric acid.

Glycerol oxidation with Bismuth Nitrate to give Meso oxalic acid.

Glycerol on oxidation with Fenton Reagent ($FeSO_4 + H_2O_2$) to give a Glycerlehyde and dihydroxy acetone.

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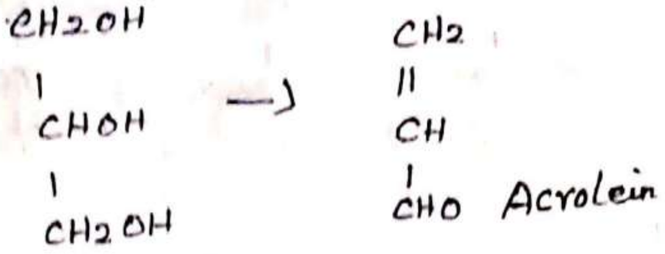
10. Dehydration



$$CH_2OH-CHOH-CH_2OH \longrightarrow CH_2=CH-CHO$$

Acrolein

Uses

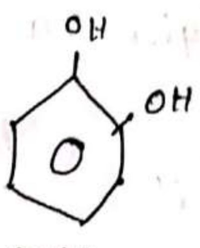
- Glyceral is used as a Homectant agent (Retaining - Moistane capacity)

Glycerol is used to prepare backery products. (Hand lotions, Shaving Creams.

It is used to prepare Synthetic polymers, plastics and in some drugs.

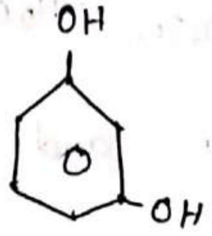
Phenols :-

The compound in which -OH is directly attached to aromatic ring is called phenols



Ortho - Cresol

Catechol



Meta Cresol.

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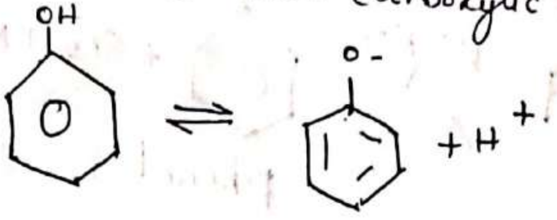
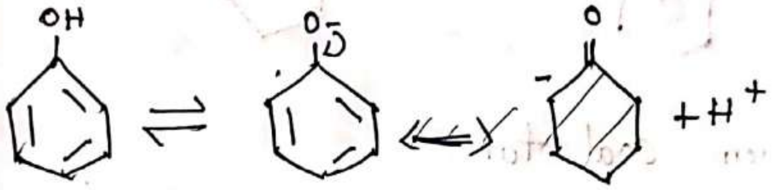
Phenol is More acidic than alcohol and less acidic than (Carboxylic acid why)

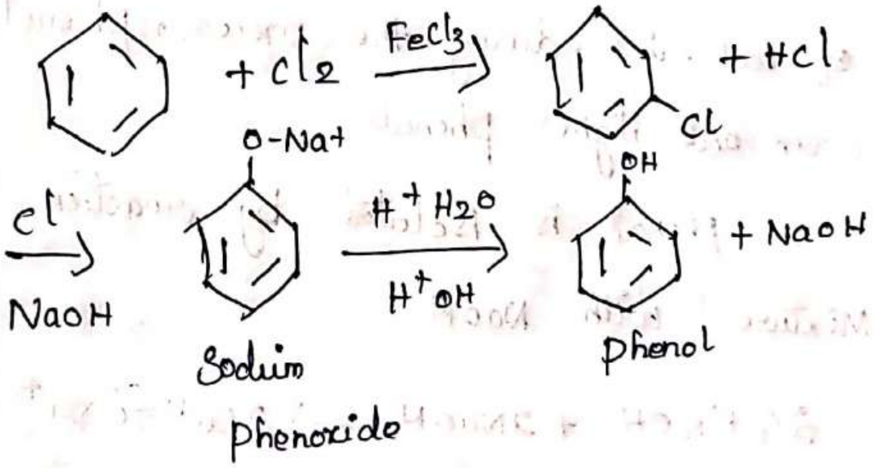


Phenol is acidic due to the formation of stable phonoxide ion in acquous solution (Due to the resonance)

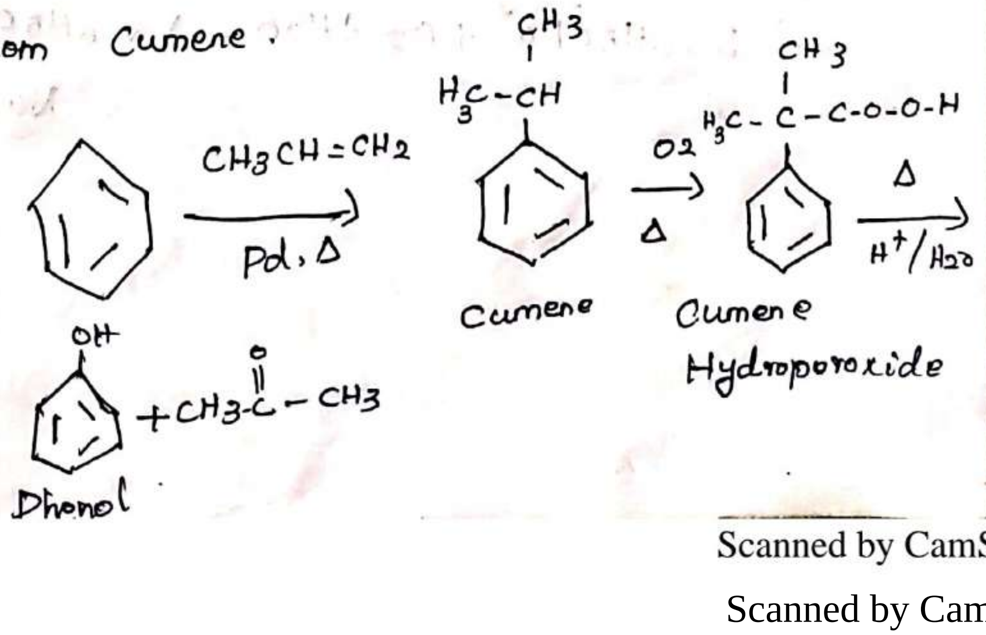


Preparation of phenol.

1) From Chlorobenzene (Dow process)



2) From Cumene.



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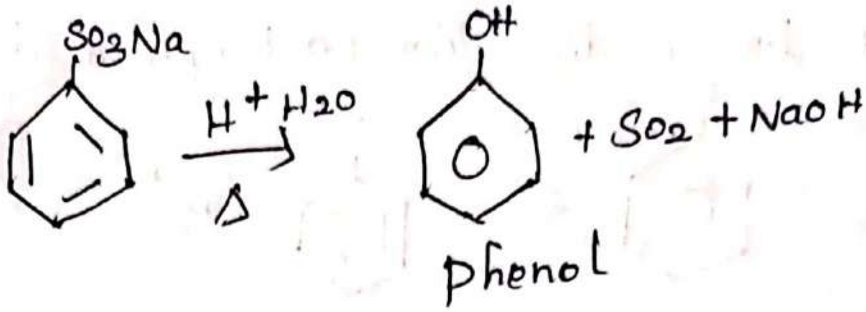
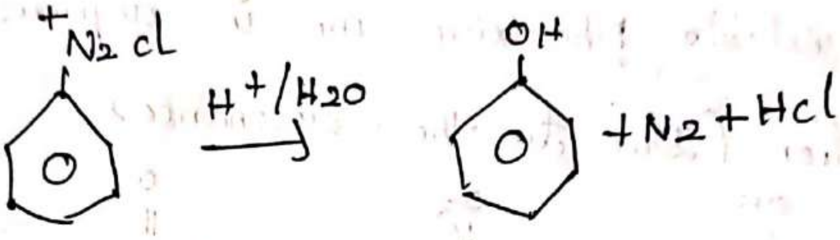
3) From benzene Sodium Sulphonate



4) From benzene diazonium chloride :



5. From coal-tar :-

Coal-tar produced about 10% of phenol

It is obtained by middle oil fuction of coal-tar, during the process, phenols, Cresols and Higher phenols.

Phenol is isolated by reaction the Mixture with NaOH.

$$2C_6H_5OH + 2NaOH \rightarrow 2C_6H_5\bar{O}Na^+ + 2H_2O$$

$$\rightarrow 2C_6H_5\bar{O}Na^+ + CO_2 + H_2O \rightarrow 2C_6H_5OH + Na_2CO_3$$

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Physical properties :-

* phenol is a colourless Gystaline Solid

* It has Melting point at 42°c , Boilling point at 182°c

* It is Hygroscopic in Nature

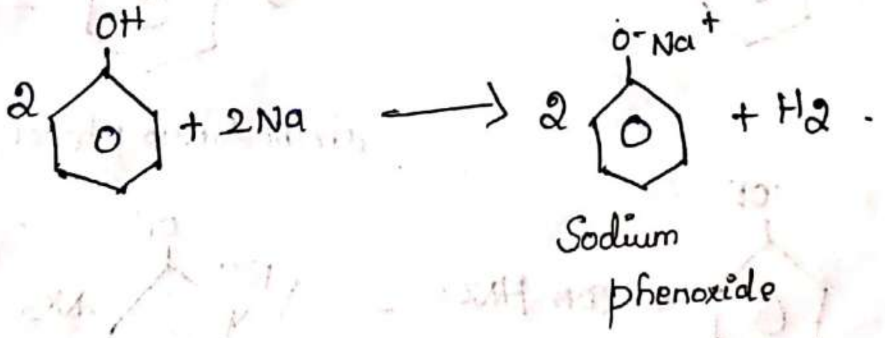
* It is insoluable in Water . Soluble in ethanol and ether

* It gives blue flourescent colour in BenZene

* It is Highly foxic , when contact with Skin it gives painful blisters .

Chemical properties .

1. Reaction on Hydroxy group :



2. Phenol react with neural Ferric Chloride to give a Violet colour Solution .

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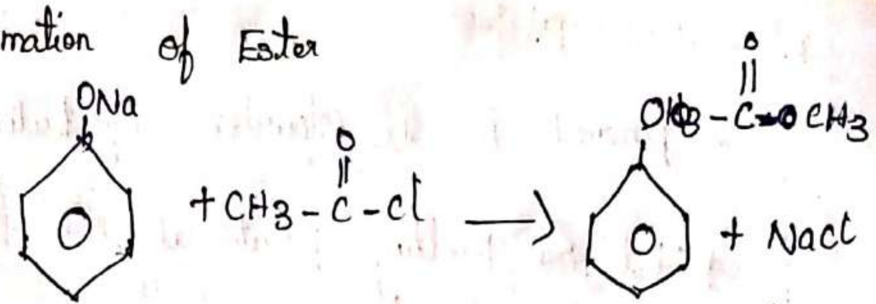
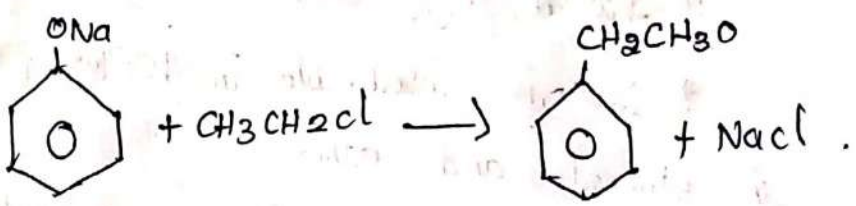
3. Formation of Ester



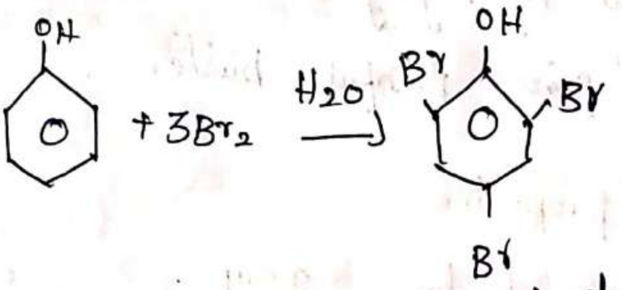
phenyl actato

4. Formation of ester



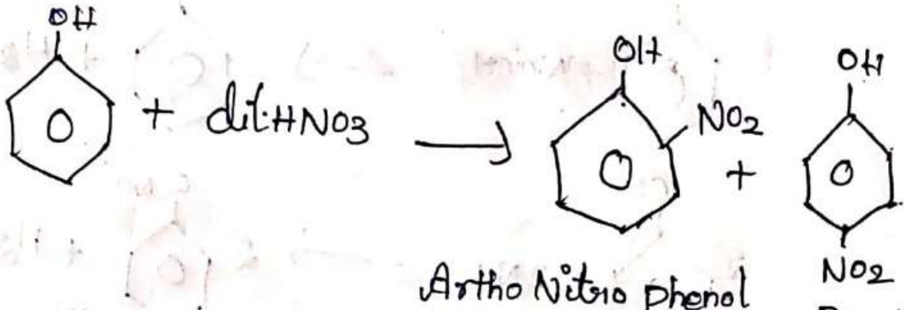
on Benzene ring .

1. Bromination



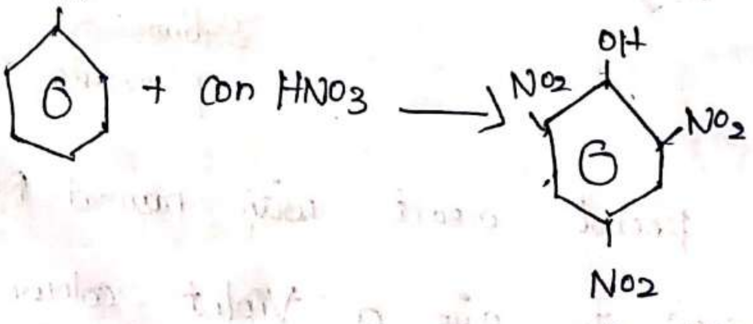
2,4,6- tribromo phenol

2. Nitration



Artho Nitro phenol

Pero N.P.



2,4,6. triNitro phenol

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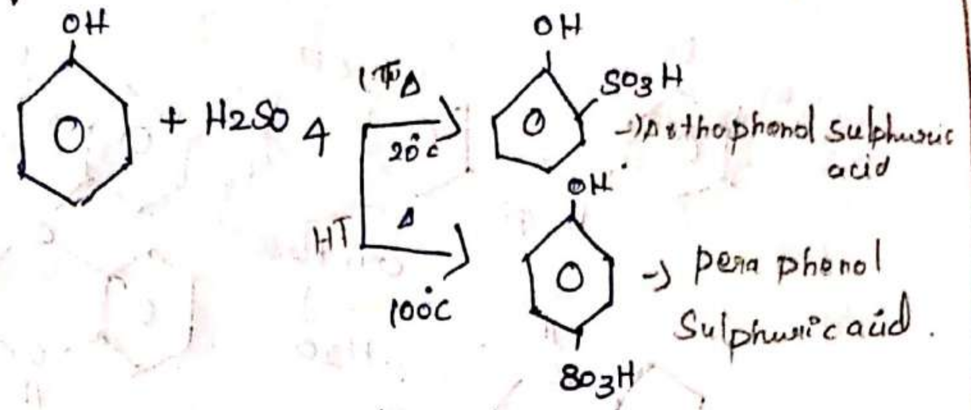
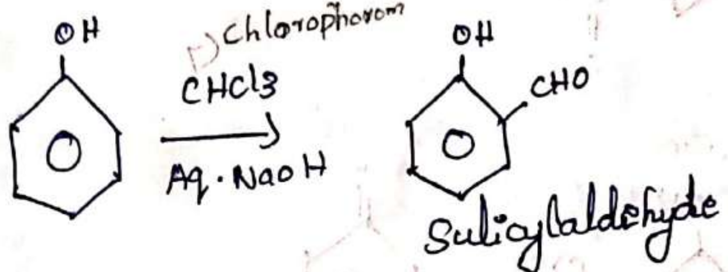
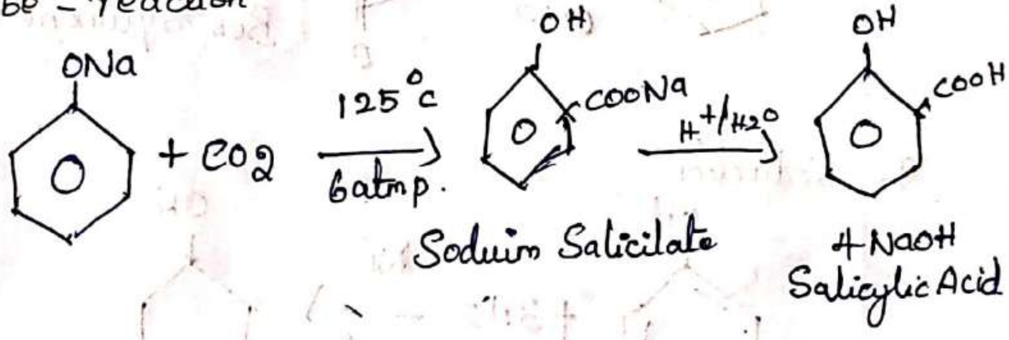
3. Sulphonation



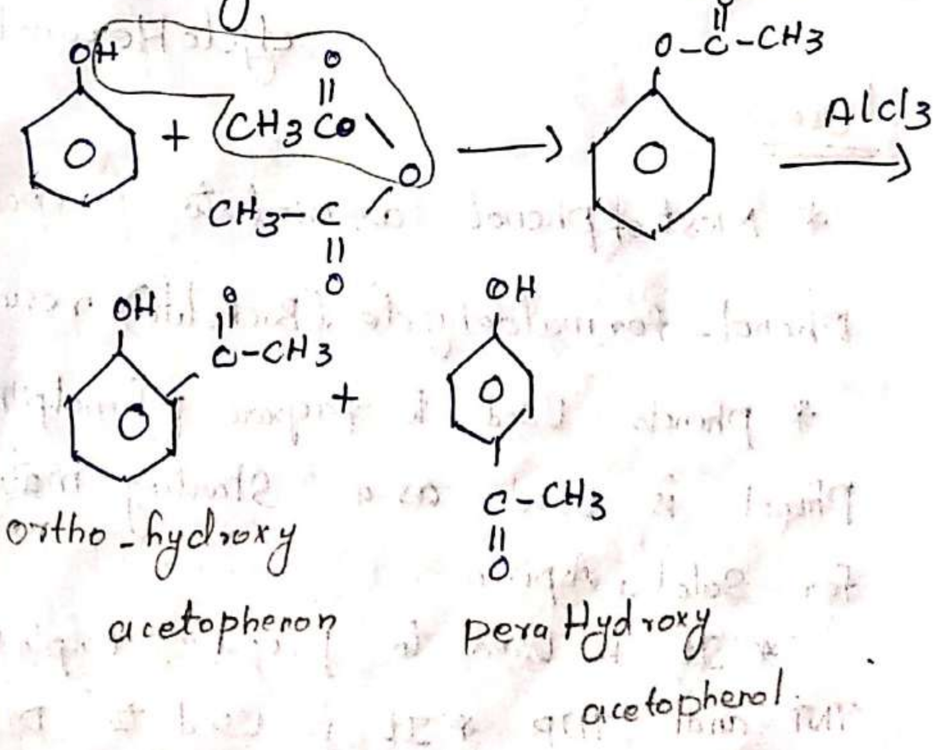
4. Reimer_ Teimann reaction (CHO).



5. Kolbe - reaction



6. Fries- rearrangement.



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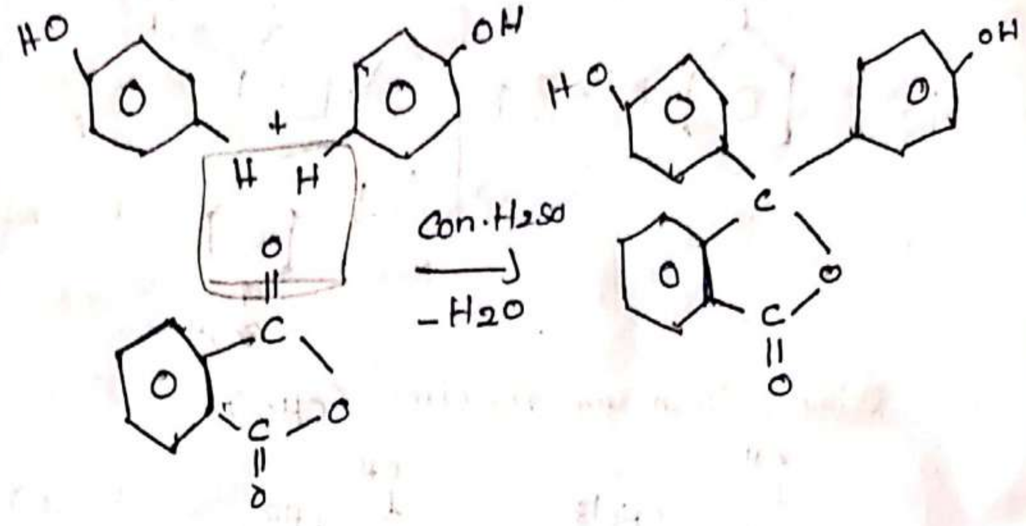
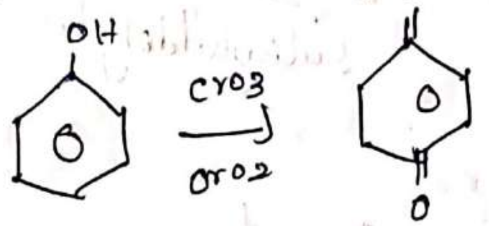
7. Reaction with phthalic Anhydride

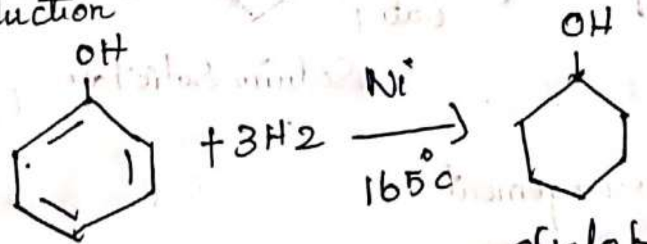


8 Oxidation



Benzoquinone.

9. Reduction



cyclo Hexanol

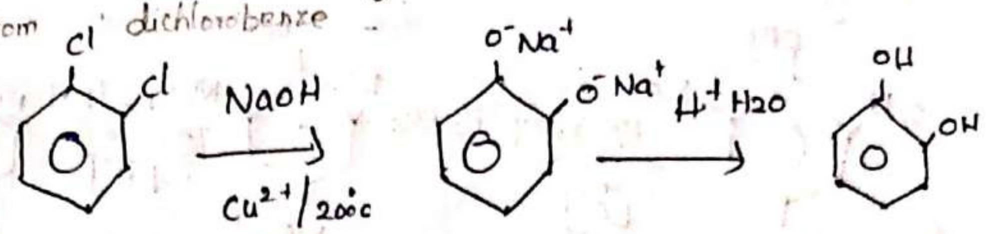
Uses

* Most of phenol are used to prepare phenol- formaldehyde (Backelite) resins.
* phenols Used to prepare phenolpthalin Phenol is Used as a Starting material for Salol, Aspirin
* It is Used to prepare explosivs like TNT and TNP. * It is Used to prepare Antiseptic.

Preparation of dihydric phenals :

From dichlorobenze

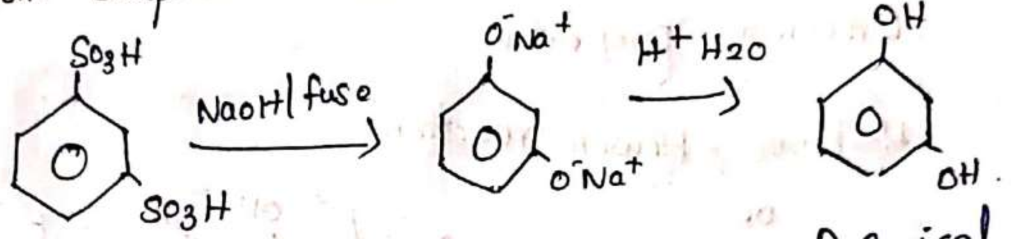
1.



Ortho-dichloro

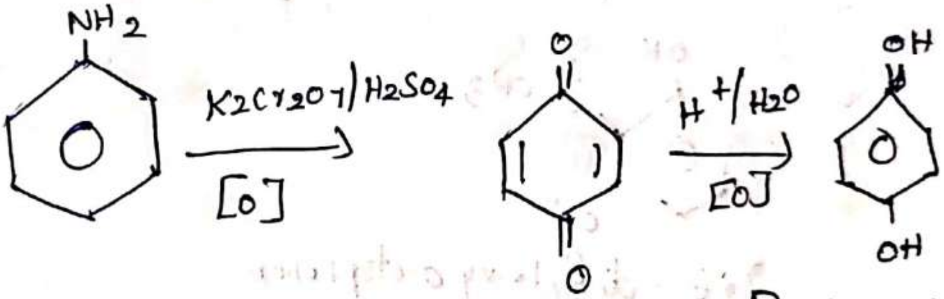
benzene

2. From Sulphuric acid.



Resorical.

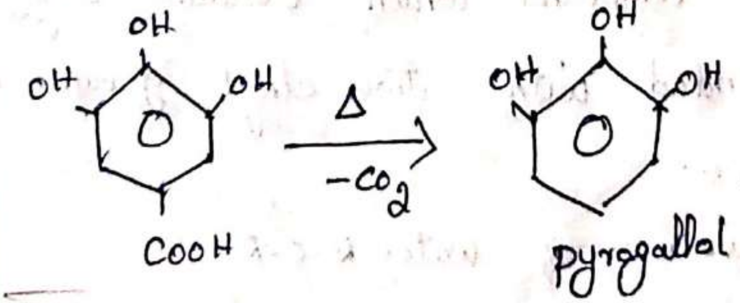
3.



P-Quinol.

Trihydric acid phenols

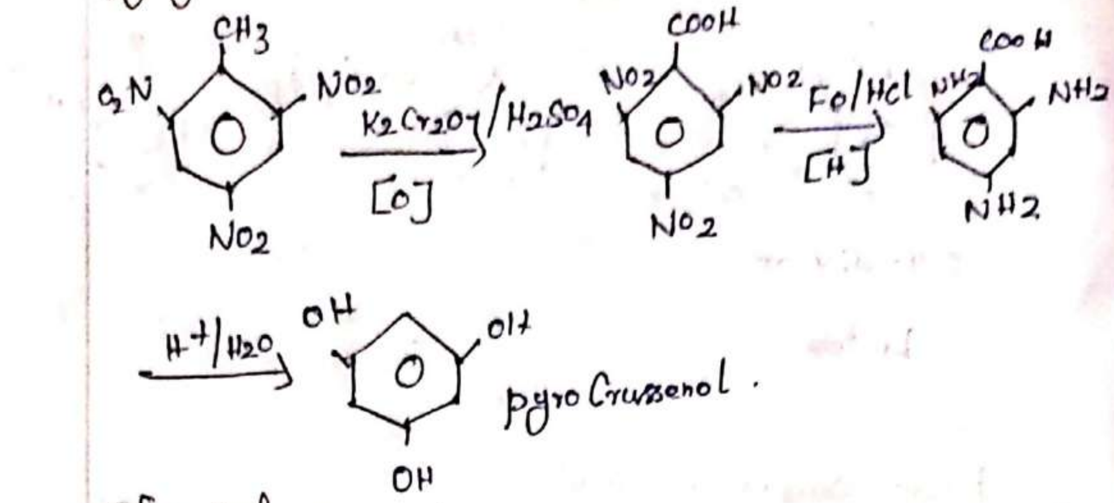
1 Pyrogallol from Gallic acid



→ * It is Used as a Starting Material

Fo detol

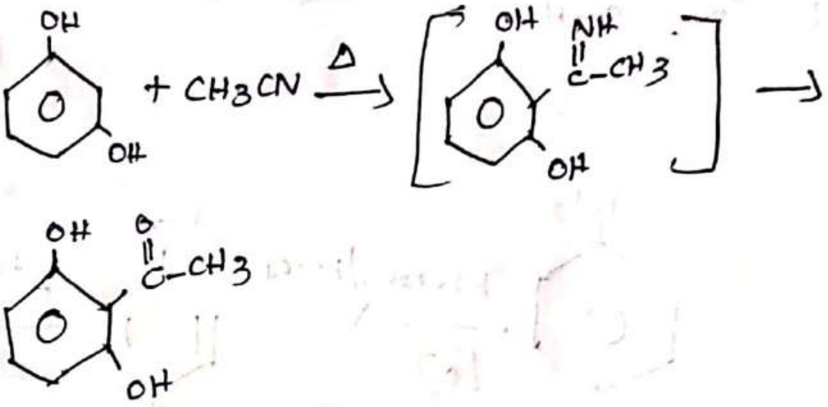
2. pyrogallol from Tri Nitro Toluene :



pyro Crussenol.

Chemical Properties :-

Haubmen - Housch reaction :-



2,6 - dihydroxy acetophenon.

Ethers (R-O-R)

The Compound which contains oxygen atom bonded with two alkyl groups are called Ethers.

Derivatives of water R-O-R

Derivatives of alcohol R-O-R

Symmetric → both alkyl groups are same

R-O-R CH_3-O-CH_3

$C_2H_5-O-C_2H_5$

Unsymmetrical - Alkyl

(R-O-R) $C_2H_5-O-CH_3$ Ethyl Methyl ether

Nomenclature :

1. Common System :

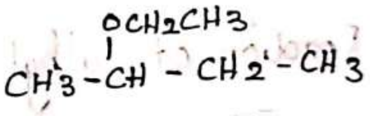
The two alkyl groups are named in alphabetical order followed by a word ether.

If both R-groups are same prefix -di is used .

Ether are named as alkoxyalkanes

$CH_3-O-CH_2CH_3$

1-ethoxy ethane



$CH_3-\underset{}{\overset{OCH_2CH_3}{CH}}-CH_2-CH_3$

2-ethoxy butane

General preparation

1. Dehydration of alcohol :

This method used to prepare symmetrical ethers

Alcohols reacts with concentrated Sulphuric acid at 140°c to give Symmetrical ethers by the removel of Water Molecule

The Alcohol used in the reacts in must be primary and the temperature must be kept at 140°c

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Ex//

$$CH_3CH_2OH + HOCH_2CH_3 \xrightarrow[140^\circ C]{Con.\,H_2So_4} CH_3CH_2-O-CH_2CH-$$

$$R-OH + R-OH \xrightarrow[140^\circ c]{Con.\,H_2So_4} R-O-R + H_2O$$

2. passing alcohol Vapour into hot Al_2O_3 tube at $250^\circ c$

$$CH_3CH_2OH + CH_3CH_2OH \xrightarrow[250^\circ c]{Al_2O_3} CH_3CH_2-O-CH_3CH_2 + H_2$$

3. Williamson Synthesis:

$$CH_3CH_2Br + CH_3CH_2O^-Na^+ \xrightarrow{\Delta} CH_3CH_2-O-CH_2CH_3$$

$$CH_3CH_2OH + NaoH \longrightarrow CH_3CH_2-ONa + H_2O$$

4. Reaction of alkyl halide with Ag_2O :-

$$\begin{array}{c} CH_3CH_2cl \\ + \\ CH_3CH_2cl \end{array} + Ag_2O \xrightarrow[2Agcl]{\Delta} CH_3CH_2-O-CH_2CH_3$$

5. Reaction of alcohol with diazomethane :

$$R-OH + CH_2N_2 \xrightarrow{HBF_2} R-O-CH_3 + N_2$$

$$CH_3CH_2-OH + CH_2N_2 \xrightarrow{HBF_4} CH_3CH_2-O-CH_2CH_3$$

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Physical properties :

* dimethyl ether and ethylmethyl ethere are gases. Other ethers are clowlers liquids

* They have pleasant odour.

* lower ethers are Highly Valatile and Highly inflammable .

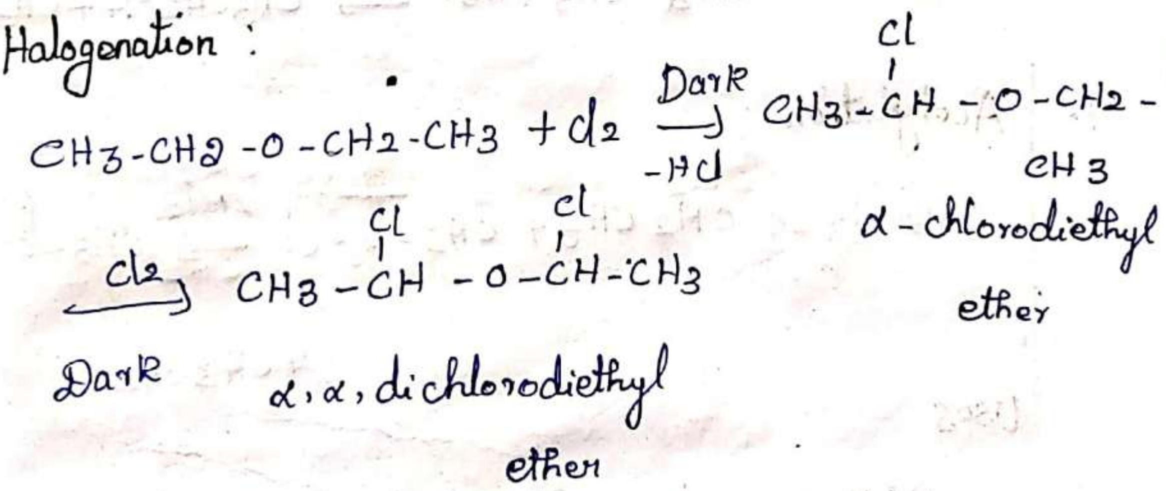
* ethers have lower boiling than isomeric alcohol

* They are insoluble in Water. Soluble in Organic Solvants Such as ethanol, chloroform, etc.

Chemical properties of ether :

1. Reaction at alkyl group :-

Halogenation :



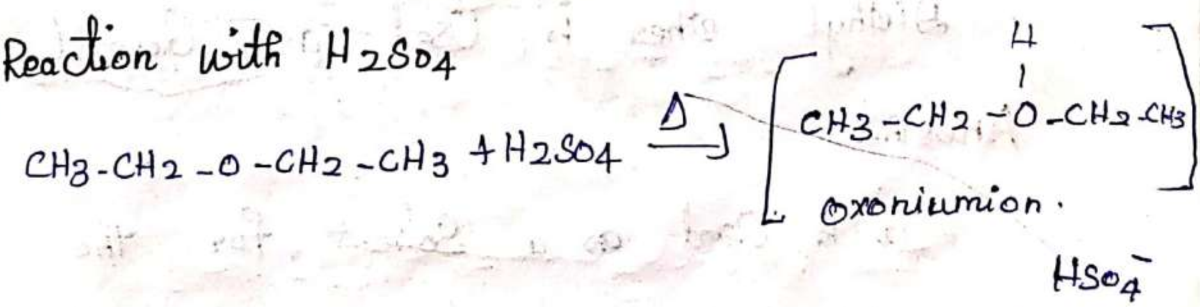
$$CH_3-CH_2-O-CH_2-CH_3 + Cl_2 \xrightarrow[-HCl]{Dark} CH_3-\overset{Cl}{\overset{|}{C}}H-O-CH_2-CH_3$$

α-chlorodiethyl ether

$$\xrightarrow[Dark]{Cl_2} CH_3-\overset{Cl}{\overset{|}{C}}H-O-\overset{Cl}{\overset{|}{C}}H-CH_3$$

α, α, dichlorodiethyl ether

2. Reaction with H_2SO_4



$$CH_3-CH_2-O-CH_2-CH_3 + H_2SO_4 \xrightarrow{\Delta} \left[CH_3-CH_2-\overset{H}{\overset{|}{O}}-CH_2-CH_3\right] HSO_4^-$$

oxoniumion.

3. Reaction with oxygen O_2 : {o-o}

$$CH_3-CH_2-O-CH_2-CH_3 \xrightarrow[\text{contact}]{\text{long}} CH_3-CH-O-CH_2-CH_3$$

Hydroperoxide of diethyl ether

4. Reaction with Water

$$CH_3-CH_2-O-CH_2-CH_3 + H_2O \xrightarrow{H^+} 2CH_3CH_2OH$$

5. Reaction with pd5 :

$$CH_3-CH_2-O-CH_2-CH_3 + PCl_5 \xrightarrow{\Delta} 2CH_3CH_2Cl + POCl_3$$

diethyl ether   2-mole of phosphrous chloride

6. Reaction with Hx :

$$CH_3CH_2-O-CH_2CH_3 + Hx \xrightarrow{\Delta} CH_3CH_2OH + CH_3CH_2x$$

$$CH_3CH_2-O-CH_2-CH_3 + HBr \xrightarrow{\Delta} CH_3CH_2OH + CH_3CH_2Br$$

7. Acetylation :

$$CH_3CH_2-O-CH_2CH_3 + CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{ZnCl_2} CH_3-\overset{O}{\overset{\|}{C}}-OCH_3. \; CH_3$$

$$+ CH_3CH_2Cl$$

Uses

Diethyl ether is Used as a General Anesthetic

It is Used as a Solvent for the preparation of grignard reagent.

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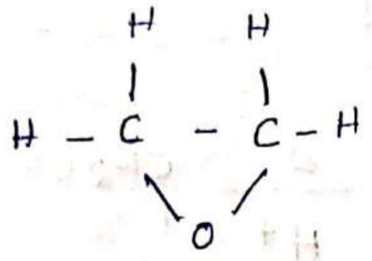
Epoxide (oxirane)

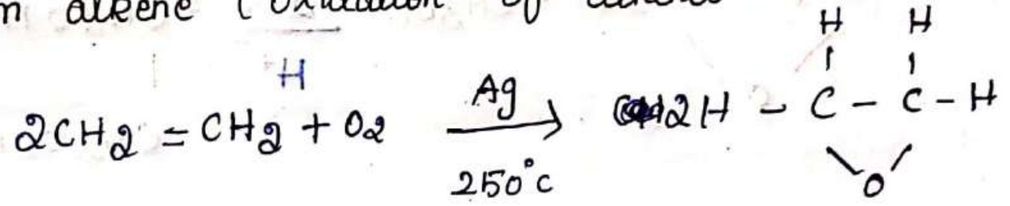


Ethylene oxide

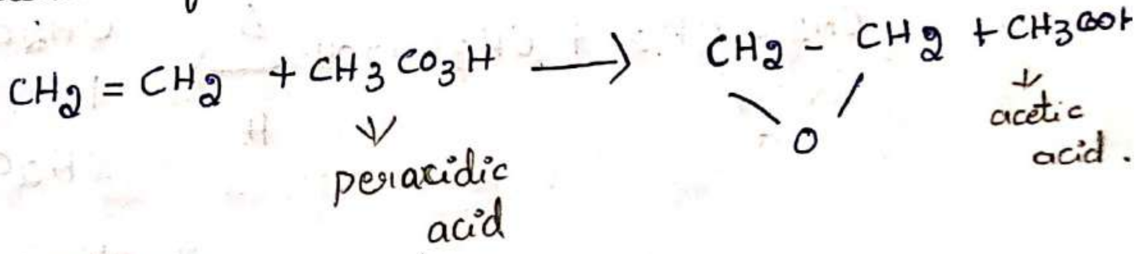
It is cyclic ether.

Preparation :

1. From alkene (oxidation of alkenes)



2) oxidation of alkenes

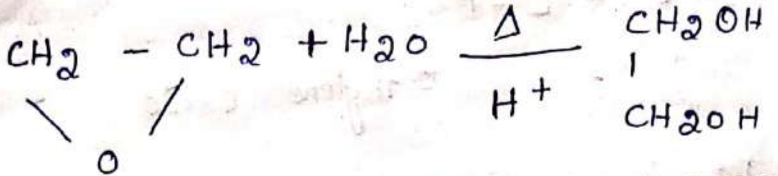


Physical properties :

- * Ethylene oxide is a toxic substance
- * It is Highly inflamable boiling point at 14°c
- * It is highly reactive
- * It undergoes ring opening reaction

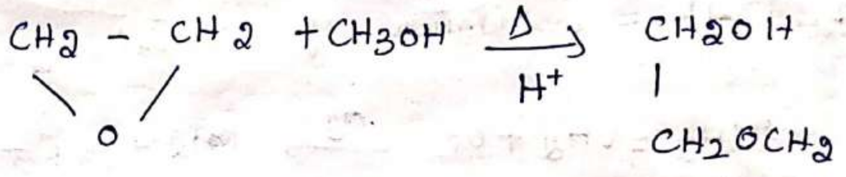
Chemical properties :

1. Reaction with Water :



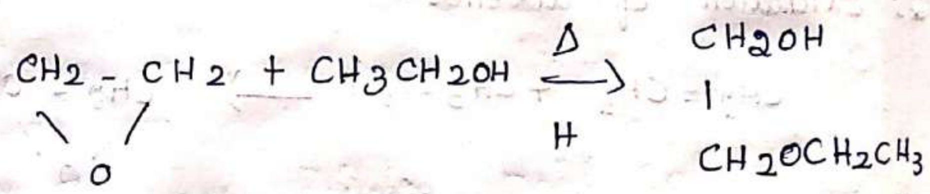
1,2 Ethane diol

2. Reaction with Methanol .



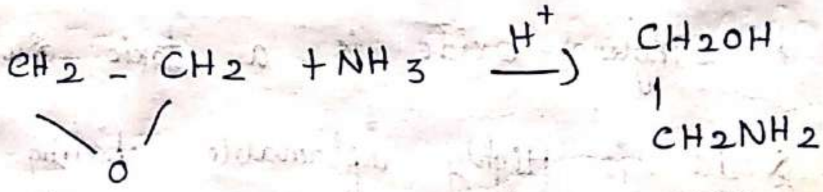
2-Methoxide ethanol

3. Reaction with ethanol



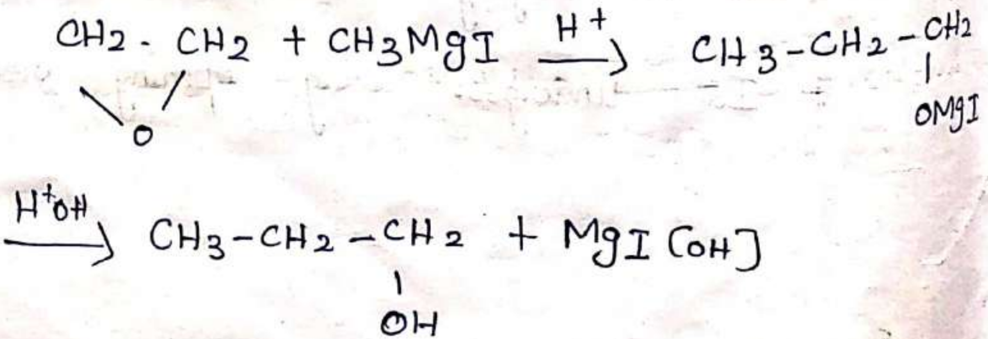
2-ethoxy ethanol

4. Reaction with NH3

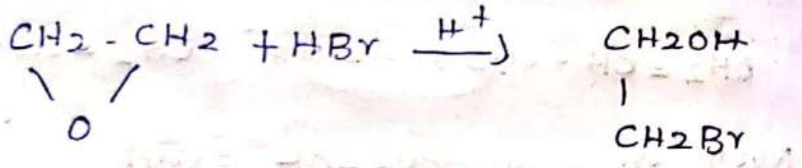


2-amioethanol

5. Reaction with Grignard Hydrogen Bromide . addition Rxn.



6. Reaction with Hydrogen Bromide:



Uses:

* It is used to prepare non - ionic detergents

* It is used to manufacture of dacron

* It is used in the preparation of Gylcernol

* It is used to prepare 2- ethoxic ethanol

* It is used in perfumes, pharmaceutical food flavours.

Unsaturated alcohols:

The compound which contain Hydroxylic group C = C

alcohols

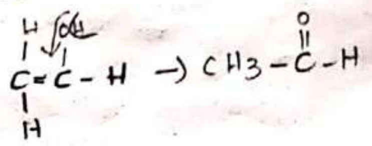
- Vinyl alcohol
- Allyl alcohol

Allyl alcohol

$CH_2=CH-CH_2-OH$

Vinyl alcohol

$CH_2=CH-OH$



$H_2C=CH-OH \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-H$

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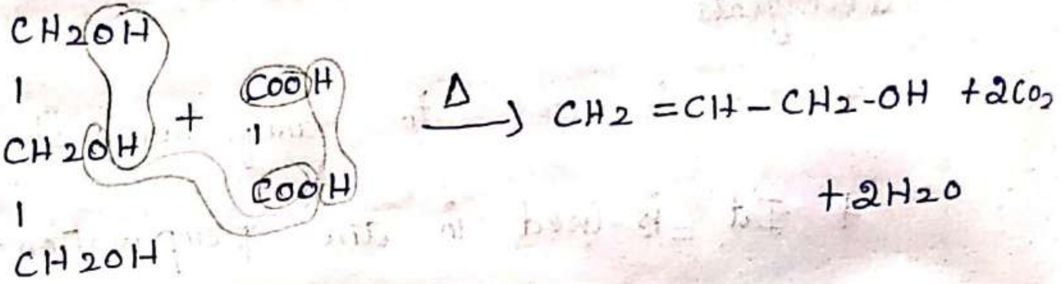
Preparation of allyl alcohol :-

1. chlorination

$$CH_2=CH-CH_3 + cl_2 \xrightarrow{500^\circ c} CH_2=CH-CH_2cl + Hcl$$

$$\xrightarrow[250^\circ c]{NaoH} CH_2=CH-CH_2-OH + Nacl$$

2. From oxalic acid.



$$\begin{matrix} CH_2OH \\ | \\ CH_2OH \\ | \\ CH_2OH \end{matrix} + \begin{matrix} COOH \\ | \\ COOH \end{matrix} \xrightarrow{\Delta} CH_2=CH-CH_2-OH + 2CO_2 + 2H_2O$$

3. Physical properties :

* It is a Clouless liquid

* It has Boiling point at 97°c

* It has charkcteristic (pangent) smell

* It is Completly ~~viss~~ Miscible with Water.

Chemical properties

1. Reaction with H_2.

$$CH_2=CH-CH_2OH + H_2 \xrightarrow[pd]{\Delta} CH_3-CH_2-CH_2OH$$

propanol

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2. Reaction with Bromide.

$CH_2=CH-CH_2-OH + Br_2 \longrightarrow CH_2Br-CHBr-CH_2OH$.

1,2-diaBromo

3. Reaction with Bromide. Sodium. Propanol

$2CH_2=CH-CH_2-OH + 2Na \xrightarrow{\Delta} 2CH_2=CH-CH_2-ONa + H_2$

4. Reaction with Hydrogen chloride.

$CH_2=CH-CH_2OH + HCl \longrightarrow \underset{\text{Allyl chloride}}{CH_2=CH-CH_2Cl} + H_2O$

5. Reaction with Acetic acid.

$CH_2=CH-CH_2OH + CH_3COOH \longrightarrow CH_2=CH-CH_2COOCH_3 + H_2O$

$CH_2=CH-CH_2OH + CH_3COOH \longrightarrow CH_2-CH-CH_2COOCH_3 + H_2O$

6. Reaction with H2OH.

$$CH_2=CH-CH_2-OH + H_2O_2 \xrightarrow{\text{dil } KMnO_4} \begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix} \text{ Glycerol}$$

7) $CH_2=CH-CH_2OH \xrightarrow[\Delta \, [O]]{Cu} CH_2=CH-CHO$

Acrolein.

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Uses :

* It used to prepare Allyl alochol, Glycerol.

* It is used to manufacture of Allyl chloride.

* It used to the preparation of Allyl halide, and perfume and drugs.

Thio alcohol (or) Thiols.

Sulfur analogues of alcohol.

R - S - H

Alkyl Hydrogen sulfide (mercaptan)

↓

To catch mercury.

CH_3SH - Methane thial (or) Methyl mercapta

CH_3CH_3SH - Ethane thial

$CH_3CH_3CH_3SH$ - Prepane thial.

Thio alcohol is weakly acidic than alcohol.

Preparation :

From Potasium . Hydrogen Sulphidate.

$$CH_3CH_2I + KSH \xrightarrow{\Delta} CH_3CH_3SH + KI.$$

Ethane thial.

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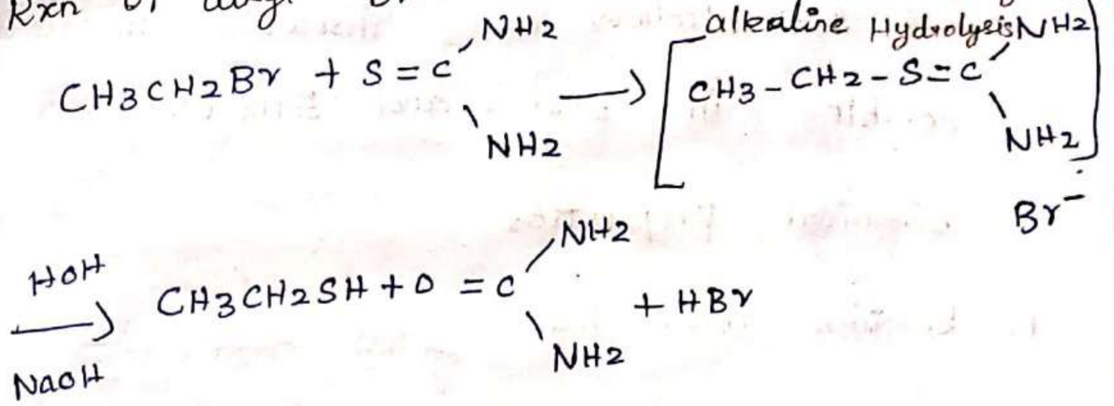
2. Rxn of alkyl Bromide wt. Thio Urea. Followed by alkaline Hydrolysis



$$CH_3CH_2Br + S=C\begin{smallmatrix}NH_2\\ NH_2\end{smallmatrix} \longrightarrow \left[CH_3-CH_2-S=C\begin{smallmatrix}NH_2\\ NH_2\end{smallmatrix}\right] Br^-$$

$$\xrightarrow[NaOH]{HOH} CH_3CH_2SH + O=C\begin{smallmatrix}NH_2\\ NH_2\end{smallmatrix} + HBr$$

Urea

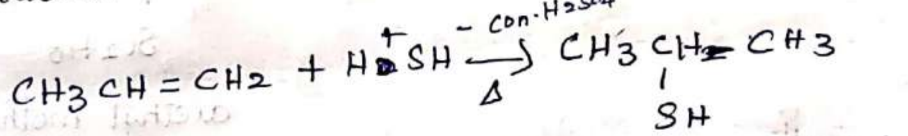
3. From Grignard reagents

$$CH_3CH_2MgBr + S \xrightarrow{\Delta} CH_3CH_2SMgBr \xrightarrow[H^+]{HOH} CH_3CH_2SH + MgBr(OH)$$

4. From passing Vapours of alcohols over H_2S in presence of Thoria (ThO_2)

$$CH_3CH_2OH + H_2S \xrightarrow{ThO_2} CH_3CH_2SH + H_2O$$

5. Reaction of alkene with H_2S presence of H_2SO_4



$$CH_3CH=CH_2 + H^+SH^- \xrightarrow[\Delta]{con.H_2SO_4} CH_3\underset{SH}{\underset{|}{CH}}-CH_3$$

propane-2-thiol

Physical properties :

* MEthane thiol is a colourless gas.

* Ethane thiol and Highed thiol are colourles Volatile liquid

* Lower thiols have characteristic Smell

* Boiling point of thiols are lesser than corresponding alcohol

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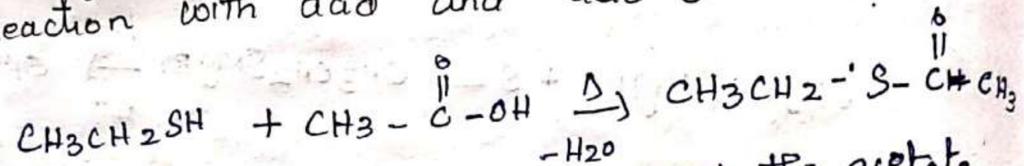
* thio alcohols are insoluble in water Soluble in EtOH, and Ethers.

chemical properties

1. Reaction with Na -

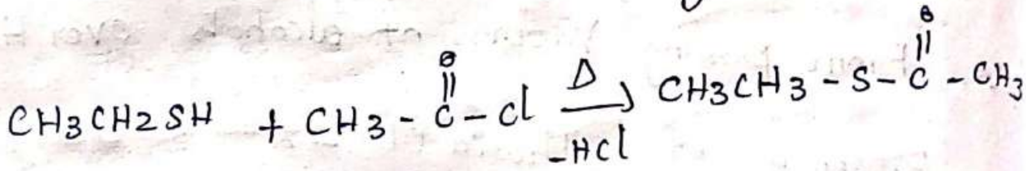
$2CH_3CH_2SH + 2Na \longrightarrow 2CH_3CH_2S^-Na + H_2\uparrow$

2. Reaction with acid and acid chloride :



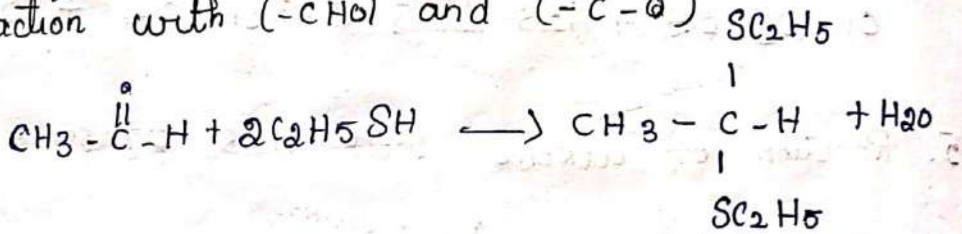
$$CH_3CH_2SH + CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[-H_2O]{\Delta} CH_3CH_2-S-\overset{O}{\overset{\|}{C}}-CH_3$$

Ethyl thio acetate.

3. 

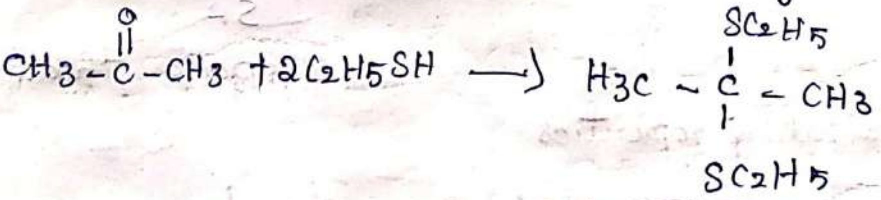
$$CH_3CH_2SH + CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[-HCl]{\Delta} CH_3CH_3-S-\overset{O}{\overset{\|}{C}}-CH_3$$

3. Reaction with (-CHO) and $(-\overset{O}{\overset{\|}{C}}-)$:



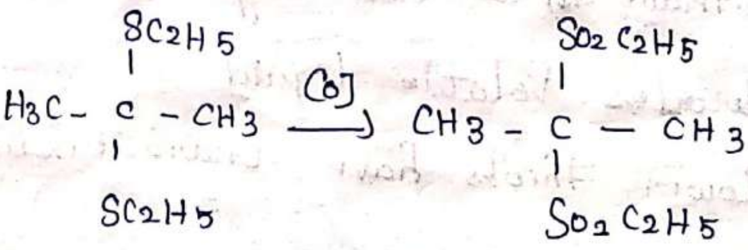
$$CH_3-\overset{O}{\overset{\|}{C}}-H + 2C_2H_5SH \longrightarrow CH_3-\underset{SC_2H_5}{\overset{SC_2H_5}{C}}-H + H_2O$$

diethyl methyl thio.



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + 2C_2H_5SH \longrightarrow H_3C-\underset{SC_2H_5}{\overset{SC_2H_5}{C}}-CH_3$$

diethyl dimethyl thiol.



$$H_3C-\underset{SC_2H_5}{\overset{SC_2H_5}{C}}-CH_3 \xrightarrow{[O]} CH_3-\underset{SO_2C_2H_5}{\overset{SO_2C_2H_5}{C}}-CH_3$$

(Sulfonal)

Reaction with base.

$$C_2H_5SH + NaOH \xrightarrow{\Delta} C_2H_5{}^-Na^+ + H_2O$$

Sodium ethyl mercaptide

Hydrolysis

$$2C_2H_5SH + 2H_2O \longrightarrow 2C_2H_5OH + 2H_2S$$

Oxidation

$$C_2H_5SH + 3[O] \xrightarrow{\Delta} C_2H_5SO_3H$$

Thio Ethers

Ether - $R-O-R$

Thio Ether - $R-S-R$

The ether are Sulfur analogues of ether.

$$CH_3-S-CH_2-CH_2-CH_3$$

(Alkyl thio Alkane)

(Methyl thio propane)

Preparation

1. Reaction of alkyl halide with K_2S

$$2C_2H_5-I + K_2S \xrightarrow{\Delta} C_2H_5-S-C_2H_5 + 2KI$$

(diethyl Sulfide)

2. Reaction of sodium Salt of ethane thiol with Alkyl halide

$$C_2H_5S^-Na^+ + CH_3I \longrightarrow C_2H_5-S-CH_3 + NaI$$

ethyl Methyl Sulfide

3. Reaction of sodium salt of ethane thiol with Alkyl Halide diethyl ethere wt P_2S_5

$$C_2H_5S^-Na^+ + CH_3I \longrightarrow C_2H_5-S-CH_3 + NaI$$

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4. Passing Vapours of thio alcohol in presence of $(Al_2O_3 + ZnS)$

$$2C_2H_5SH \xrightarrow[300°C]{Al_2O_3/ZnS} C_2H_5-S-C_2H_5 + H_2S$$

physical properties.

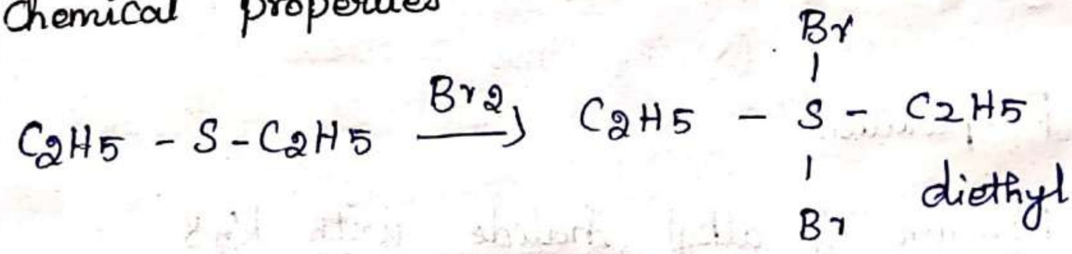
* Unpleasent Smelling

* boiling point of thio ether of higher than the corresponding ether

* thio ether are insoluble in Water

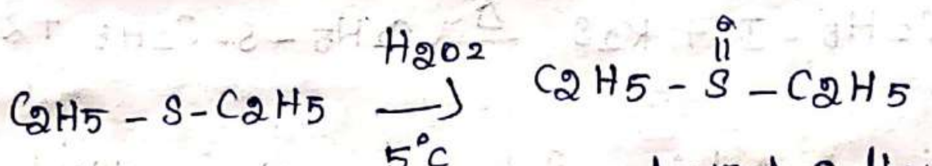
* thio ether are Soluble in organic Solvend (ethanol)

Chemical properties

1. 

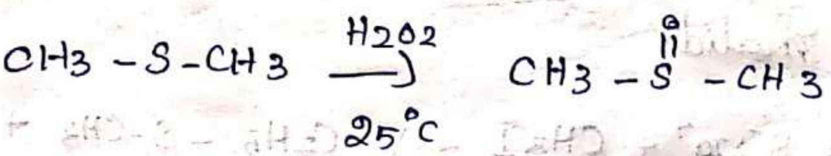
$$C_2H_5-S-C_2H_5 \xrightarrow{Br_2} C_2H_5-\underset{Br}{\overset{Br}{S}}-C_2H_5$$

diethyl dibrom thio

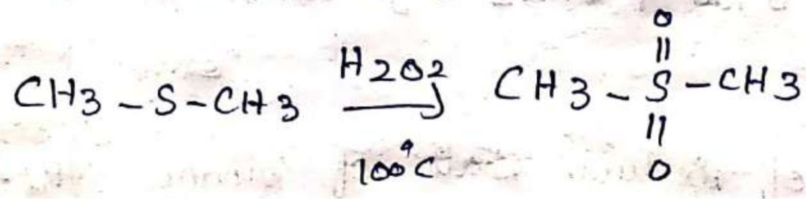
2. 

$$C_2H_5-S-C_2H_5 \xrightarrow[5°C]{H_2O_2} C_2H_5-\overset{O}{\overset{\|}{S}}-C_2H_5$$

diethyl Sulboxide



$$CH_3-S-CH_3 \xrightarrow[25°C]{H_2O_2} CH_3-\overset{O}{\overset{\|}{S}}-CH_3$$



$$CH_3-S-CH_3 \xrightarrow[100°C]{H_2O_2} CH_3-\underset{O}{\underset{\|}{\overset{O}{\overset{\|}{S}}}}-CH_3$$

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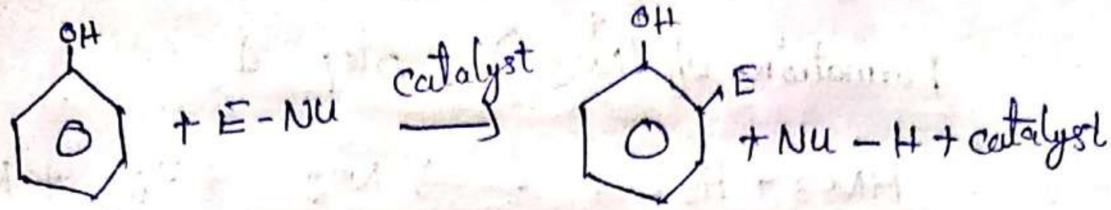
Electrophilic Substitution Reaction in phenol



Hydrogen atom in phenol is replaced by electrophile is known as electrophilic substitution Reaction

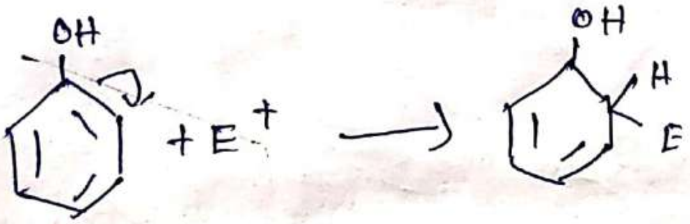
Mechanism

Step : 1

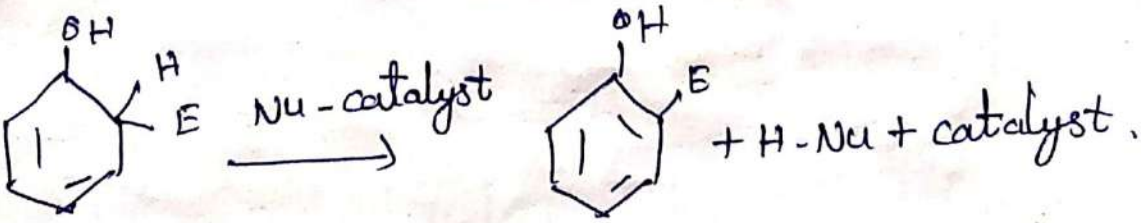
Formation of (E^+) step-1

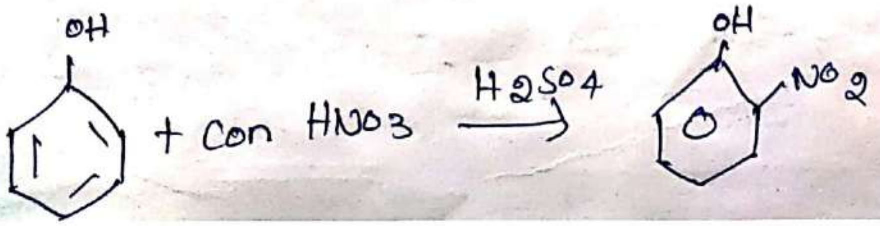
$$E^+ - Nu^- \xrightarrow{catalyst} E^+ + Nu - catalyst.$$

Step 2



Step 3 : loss of porton





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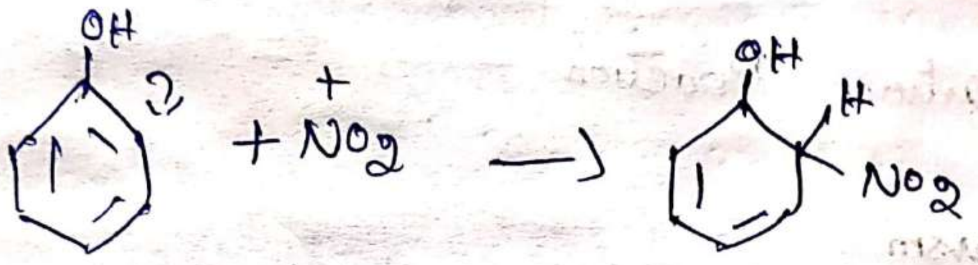
Step - 1

Formation of ($\overset{+}{N}O_2$) Step - 1

$HNO_3 + H_2SO_4 \longrightarrow \overset{+}{N}O_2 + H_2O + H\bar{S}O_4$

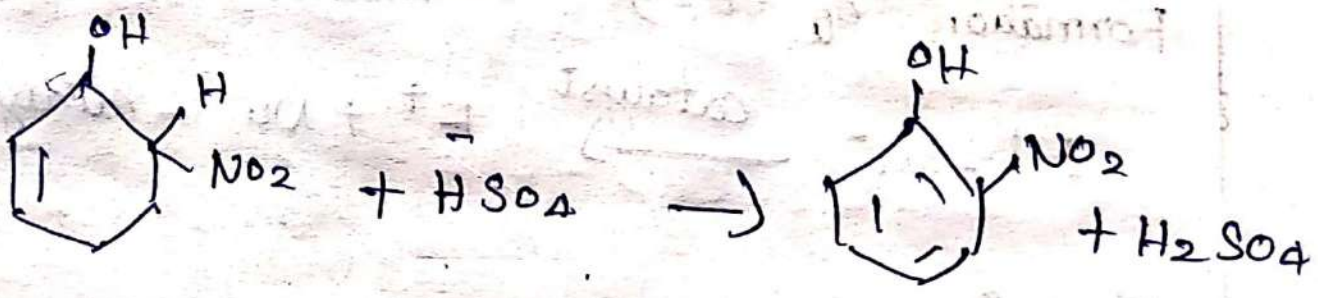
Step - 2

Attrack of electrophile ($\overset{+}{N}O_2$)



Step - 3

loss of proton



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2. Organometallic compounds

Organometallic Compounds.

An Organic Compound in which a metal is diectly attached to Carbon atom is known as Organometallic Compounds.

Organic + Metal → Organometallic

Organic, Inorganic, hybrid Compounds.

Versatile reagents in Organic Synthesis

Classification of organometallic Compound.

* Simple Organometallic Compound
* Complex Organometallic Compound.

Simple organometallic compound.

R - M - R — $CH_3 - Zn - CH_3$

↓

Covalent bond — di ~~eth~~ methyl zinc

Complex organometallic compound.

Ionic bond.

R - M - X — CH_3MgBr

↓ ↓ ↓

Alkyl Metal Halides — ethyl Megnisium bromide.

Organo Megesium Compound.

R - Mg - X (General formula)

It polar in Nature

Grignard reagents

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In 1912 He got awarded nobel prize for them Tremendous applications of organomegnesium Compound in Organic Synthesis.

Preparations of Grignard reagent (or) organomagnesium Compound.

$R-X + Mg \xrightarrow[\text{Reflux}]{\text{Ether}} R + MgX$ Alkyl Magnesium halides

$CH_3-Br + Mg \xrightarrow[\text{Reflux}]{\text{Ether}} CH_3-Mg-Br$ methyl Magnesium Bromide

$CH_3CH_2-Br + Mg \xrightarrow[\text{Reflux}]{\text{Ether}} CH_3CH_2-Mg-Br$ Ethyl Magnesium Bromide

Mechanism

Reactivity

1) Free radicals Mechanism.

$I > Br > Cl > F$

$2R-X + Mg \rightarrow R-R + MgX_2$ $CH_3 > C_2H_5 > C_3H_7$

$Mg + MgX_2 \rightarrow 2\dot{M}gX$

$R-X + \dot{M}gX \xrightarrow{\text{Homolytic bond creation}} R^{\cdot} + MgX_2$

$R^{\cdot} + \dot{M}gX \rightarrow RMgX$

Reaction of organometallic Compounds :-

① Reaction with compounds containing active Hydrogen.

$R-Mg-X + HOH \rightarrow R-H + Mg(OH)X$

$CH_3-Mg-Br + HOH \rightarrow CH_4 + Mg(OH)Br$

$CH_3CH_2MgBr + HOH \rightarrow CH_3CH_3 + Mg(OH)Br$

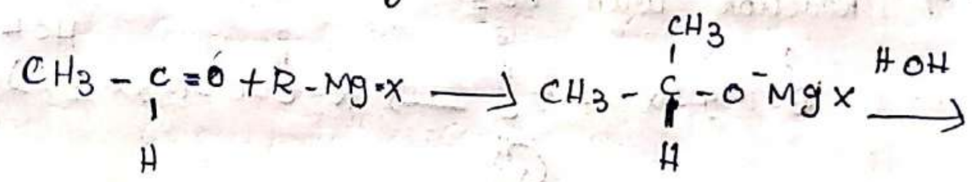
2. Reaction with alcohols :-

$R-Mg-X + R-OH \rightarrow R-R + Mg(OH)X$

$CH_3-Mg-Br + CH_3-OH \rightarrow \underset{\text{Ethane}}{CH_3-CH_3} + Mg(OH)Br$

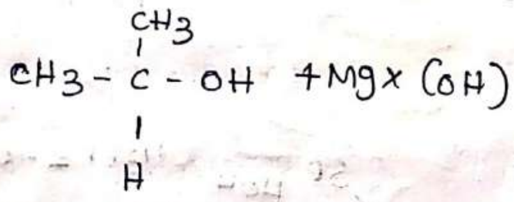
$CH_3CH_2-Mg-Br + CH_3-OH \rightarrow \underset{\text{Broane.}}{CH_3CH_2CH_3} + Mg(OH)Br$

3. Reaction with Carbonyl Compound. ($>C=O$)

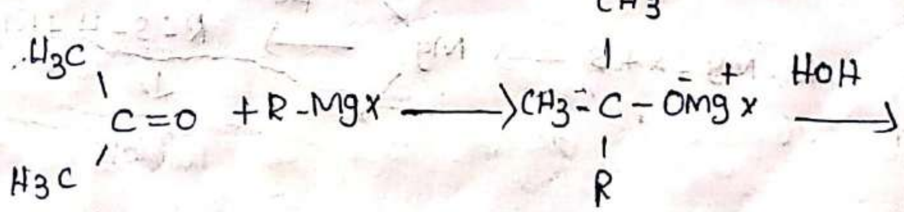


$$CH_3-\underset{\displaystyle H}{\underset{|}{C}}=O + R-Mg-X \rightarrow CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle H}{\underset{|}{C}}}}-O^-MgX \xrightarrow{HOH}$$

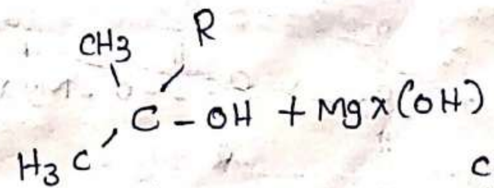
Carbon which react as a nucleophilic



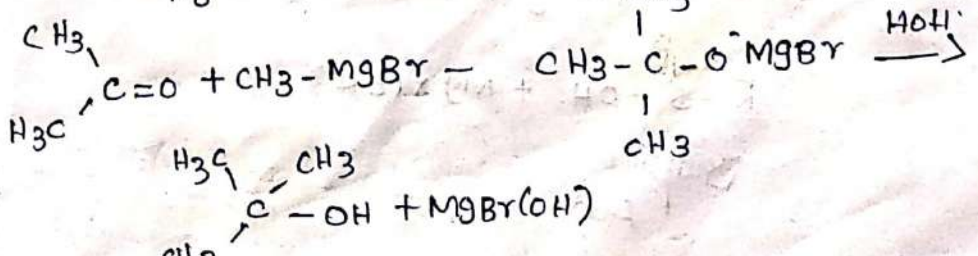
$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle H}{\underset{|}{C}}}}-OH + MgX(OH)$$



$$\begin{matrix}H_3C\\ H_3C\end{matrix}\!\!>C=O + R-MgX \rightarrow CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle R}{\underset{|}{C}}}}-OMgX \xrightarrow{HOH}$$



$$\begin{matrix}CH_3\ \ R\\ H_3C\end{matrix}\!\!>C-OH + MgX(OH)$$



$$\begin{matrix}CH_3\\ H_3C\end{matrix}\!\!>C=O + CH_3-MgBr \rightarrow CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-O^-MgBr \xrightarrow{HOH}$$

$$\begin{matrix}H_3C\ \ CH_3\\ CH_3\end{matrix}\!\!>C-OH + MgBr(OH)$$

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③ Reaction with epoxides

$$R-Mg-X + \underset{\diagdown O \diagup}{CH_2-CH_2} \rightarrow R-CH_2-CH_2-\bar{O}-MgX \xrightarrow{HOH}$$

$$R-CH_2-CH_2-OH + MgX(OH)$$

$$CH_3-Mg-Br + \underset{\diagdown O \diagup}{CH_2-CH_2} - CH_3-CH_2-CH_2-\bar{O}-MgBr$$

$$\xrightarrow{HOH} CH_3-CH_2-CH_2-OH + MgBr(OH)$$

$$CH_3MgBr + \underset{\diagdown O \diagup}{CH_2-CH}-CH_3 \rightarrow [CH_3-CH_2-\underset{|\,O^--MgBr}{CH}-CH_3$$

$$\xrightarrow{HOH} CH_3-CH_2-CH-CH_3-OH + MgBr(OH)$$

4. Reaction with CO_2

$$\overset{\delta-}{R}-\overset{\delta+}{Mg}-X + \underset{\overset{\|}{O}}{\overset{\overset{O}{\|}}{C}} \rightarrow R-\overset{\overset{O}{\|}}{C}-O^--MgX \xrightarrow{HOH}$$

$$R-\overset{\overset{O}{\|}}{C}-OH + MgX(OH)$$

Carboxylic Acid.

5. Reaction with S

$$R-Mg-X + S \rightarrow Mg\begin{matrix} \diagup SR \\ \diagdown X \end{matrix} \xrightarrow{HOH} R-S-H + MgX(OH)$$

$\downarrow$

Thiols.

6 Reaction SO_2

$$R-Mg-X + \underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}} \rightarrow R-\overset{\overset{O}{\|}}{S}-O^--\overset{+}{Mg}X \xrightarrow{HOH}$$

$$R-\overset{\overset{O}{\|}}{S}-OH + MgX(OH)$$

Sulfinic Acid

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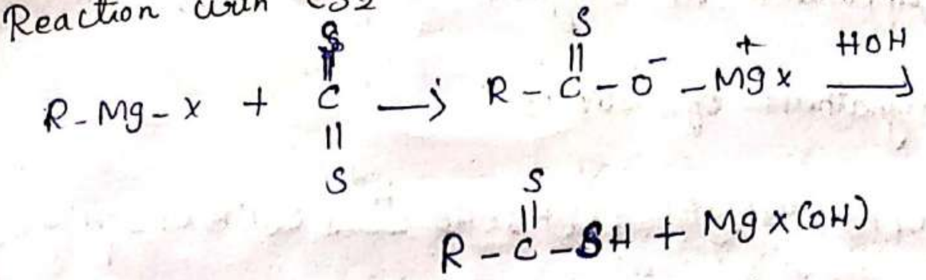
7. Reaction with CS_2



$$R-Mg-x + \overset{S}{\overset{\|}{\underset{\underset{S}{\|}}{C}}} \longrightarrow R-\overset{S}{\overset{\|}{C}}-O^{-}-\overset{+}{Mg}x \xrightarrow{HOH} R-\overset{S}{\overset{\|}{C}}-SH + Mgx(OH)$$

Dithio Acid.

8. Reaction with I

$$R-Mg-x \xrightarrow{I_2} R-I + Mgx(I)$$

$$CH_3-Mg-Br \xrightarrow{I_2} CH_3-I + MgBr(I)$$

9. Reaction with Metal halides

$$4CH_3CH_2MgBr + pbcl_4 \longrightarrow (CH_3CH_2)_4Pb + 4MgBrcl$$

(TEL) Anti knocking Agent

$$2CH_3CH_2MgBr + Hgcl_2 \longrightarrow (CH_3CH_2)_2Hg + 2MgBrcl$$

$$4CH_3MgBr + Sicl_4 \longrightarrow (CH_3)_4Si + 4MgBrcl$$

Tetra Methyl Silin

$$3CH_3MgBr + Pcl_3 \longrightarrow (CH_3)_3P + 3MgBrcl$$

10. Reaction with Alkyl Halide:

$$CH_3CH_2MgBr + CH_3CH_2cl \longrightarrow CH_3CH_2CH_2CH_3 + MgBrcl$$

Physical properties.

- * Grignard regent act as strong Alkalis
- * Grignard regent act as a nucleophile
- * It should be kept in dry environment
- * If it is conducted with water Grignard regent destroyed

Application of Grignard reagent.

1). Synathesis of stilbone :-

$$C_6H_5CH_2MgBr + C_6H_5CHO \xrightarrow{H^+} C_6H_5CH_2\underset{OH}{\underset{|}{CH}}-C_6H_5$$

Benzyl MgBr   Benzoldehyde

$$\xrightarrow[-H_2O]{\Delta} C_6H_5-CH=CH-C_6H_5$$

Stilbene

2. Synathesis of ether.

Methoxy methyl cl

$$CH_3CH_2MgBr + CH_3OCH_2Cl \longrightarrow CH_3CH_2CH_2-O-CH_3$$

Methyl propyl ether $+ MgBrCl$

3. Synathesis of Alkane :-

$$CH_3CH_2MgBr + CH_3CH_2Cl \longrightarrow CH_3CH_2-CH_2-CH_3 + MgBrCl$$

$$CH_3CH_2MgBr + HOH \longrightarrow CH_3CH_3 + MgBr(OH)$$

4. Synathesis of Alkyl ~~&~~ Cynai Cyanide :-

$$CH_3CH_2MgBr + \overset{CN-CN}{\cancel{CH_3CH_2CN}} \longrightarrow CH_3CH_2-\overset{(CN)}{CH_2-CH_3}$$

Cyno ethane $+ MgBr(CN)$

Grignard reagent act as nucleophile to Synathesis Many Organic Compounds.

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Organozinc Compounds (R_2Zn)

$R - Zn - R$ => dialkylzinc

↓

Alkyl (or) Aryl

* First Synthesized Organometallic Compounds

* It is Very important in Organic Sythesis.

Preparation

1. From alkyl halide :

$R-X + 2Li \xrightarrow{\text{Inert atmosph}}$

$R-X + Zn \longrightarrow R-ZnX$

$2R-ZnX \longrightarrow R_2Zn + ZnX$

Alkyl Halide react with Zinc And gives Alkyl or Aryl zinc

Alkyl Zinc Iodite react together to form OrganoZinc Compound.

2. From Trialkyl aluminium.

$2R_3Al + ZnX_2 \longrightarrow R_2Zn + 2R_2AlX$

$2R_3Al + ZnCl_2 \longrightarrow R_2Zn + 2R_2AlCl$.

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physical properties

Organozic Compounds are less polar than Grignard reagent.

It is low Boiling Liquids are low Melting Soils.

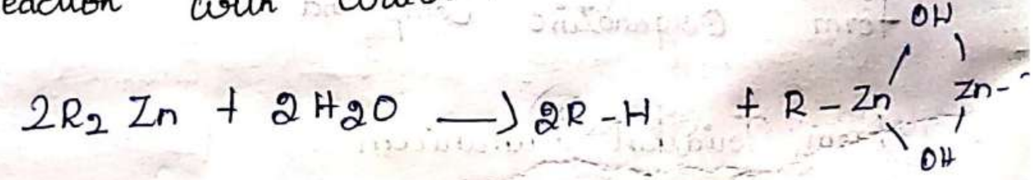
It is Highly inflamable in air

It is insoluble in Water. It is Soluble in Organic Compounds.

* Reactivity of OrganoZinc Compounds are Much less than Organomegnisum Compounds.

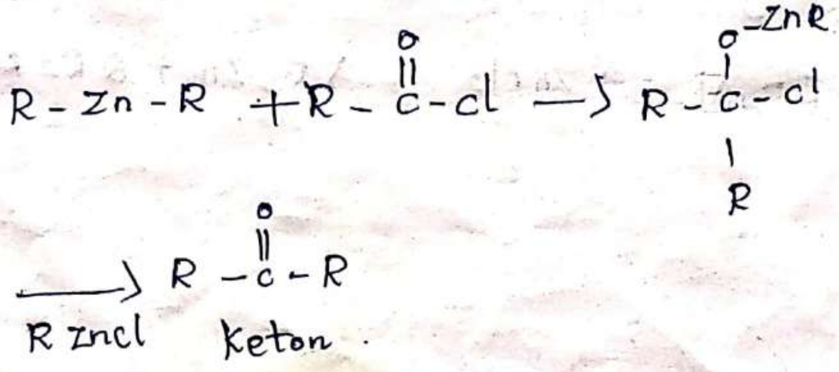
Chemical properties

1) Reaction with Water.



$$2R_2Zn + 2H_2O \longrightarrow 2R-H + R-Zn \begin{matrix} -OH \\ \\ OH \end{matrix} Zn-$$

2) Reaction with acid chloride :-



$$R-Zn-R + R-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow R-\underset{R}{\underset{|}{\overset{O-ZnR}{\overset{|}{C}}}}-Cl$$

$$\xrightarrow[RZnCl]{} R-\overset{O}{\overset{\|}{C}}-R$$

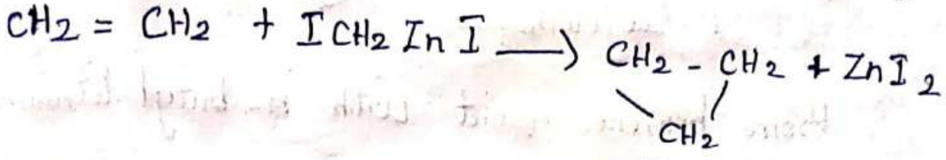
Keton.

3. Reaction with alky halide.

$R_2-Zn + CH_3CH_2Cl \longrightarrow R-CH_2-CH_3 + RZnCl$

Higher alkanes.

4. Reaction with iodo metal Zinc Chloride



$CH_2=CH_2 + ICH_2ZnI \longrightarrow \underset{CH_2}{CH_2-CH_2} + ZnI_2$

cyclo propane.

Organolithium Compounds

(R-Li)

The lithium is directly attached with carbon.

Characterised by carbon -Li bond.

$\overset{\delta-}{C}-\overset{\delta-}{Li}$

↙

Nuclophile

- * Act as a powerful nuclophiles
- * It is also act as a base
- * It is Highly Reactive than grignard reagent.
- * It is Used as a important source in Organic Synthesis.

Preparation.

1) From Alkyl or Aryl halides

$R-X + 2Li \longrightarrow R-Li + LiX$

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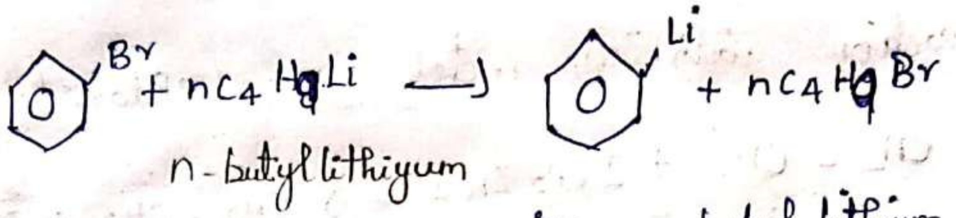
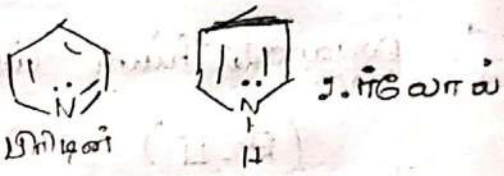
2. Halogen exchanged methode.

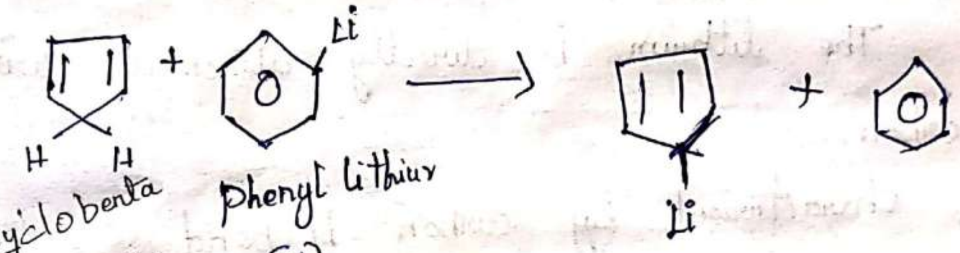
$R-X + R'-Li \rightarrow R-Li + R'-X$



Bromo benzene react with n- butyl lithium to form a lithuim Benzene.



3. Metalation



cyclobenta diene. Phenyl lithiur (or) Lithium Benzene

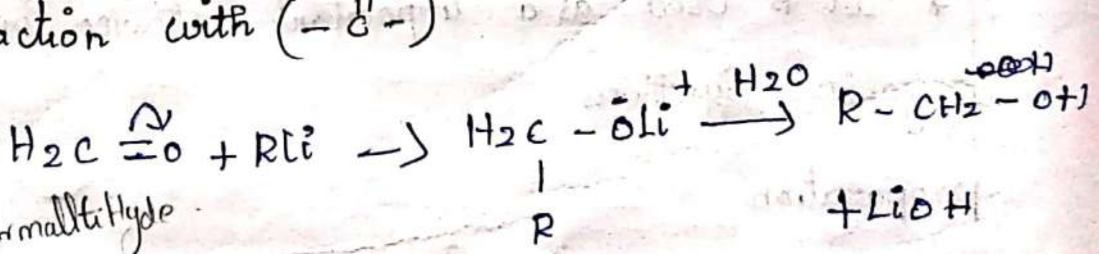
Chemical properties

1. Reaction with H_2O

Alkane

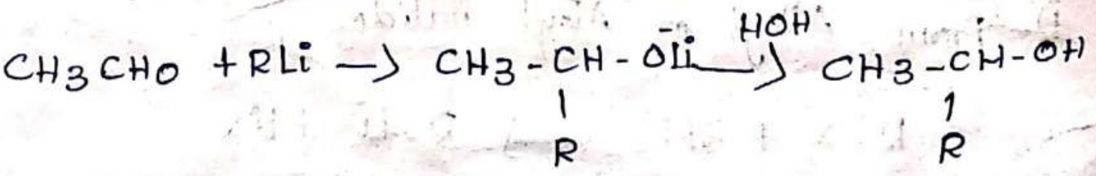
$R-Li + H_2O \rightarrow R-H + LiOH$

2. Reaction with $(-\overset{O}{\overset{\|}{C}}-)$



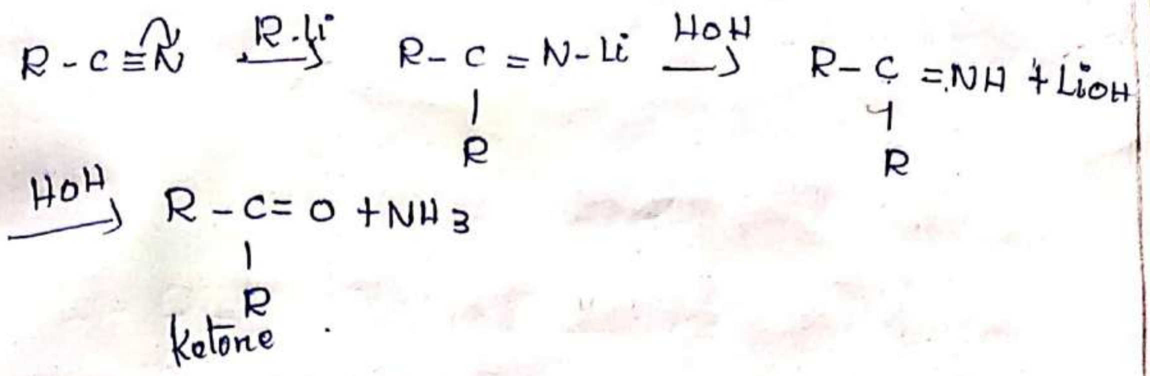
$$H_2C=O + RLi \rightarrow \underset{R}{\underset{|}{H_2C}}-OLi \xrightarrow{+H_2O} R-CH_2-OH + LiOH$$

Formalltillyde



$$CH_3CHO + RLi \rightarrow CH_3-\underset{R}{\underset{|}{CH}}-OLi \xrightarrow{HOH} CH_3-\underset{R}{\underset{|}{CH}}-OH$$

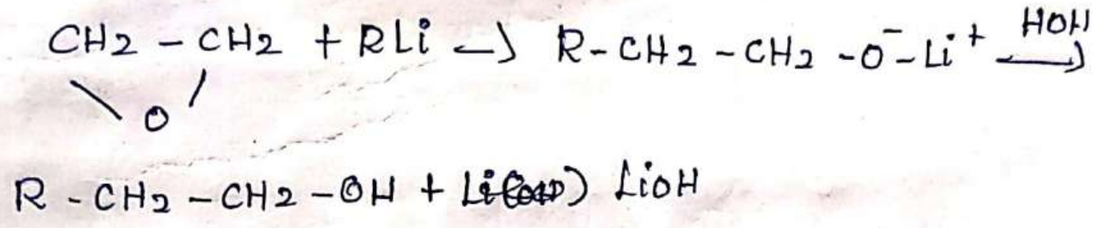
3. Reaction alkyl Cyanide



$$R-C\equiv N \xrightarrow{R\text{-}Li} \underset{R}{\underset{|}{R-C}}=N-Li \xrightarrow{HOH} \underset{R}{\underset{|}{R-C}}=NH + LiOH \xrightarrow{HOH} \underset{R}{\underset{|}{R-C}}=O + NH_3$$

Ketone.

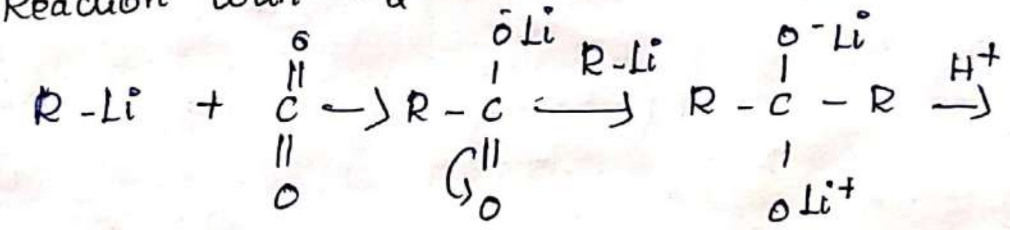
4. Reaction with epoxides



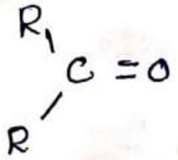
$$CH_2-CH_2 \,(\text{-O-}) + RLi \rightarrow R-CH_2-CH_2-O^--Li^+ \xrightarrow{HOH}$$

$$R-CH_2-CH_2-OH + \cancel{Li(OH)}\ LiOH$$

5. Reaction with CO_2



$$R-Li + O=C=O \rightarrow R-\overset{O^-Li}{\overset{|}{C}}=O \xrightarrow{R\text{-}Li} R-\underset{OLi^+}{\underset{|}{\overset{O^-Li}{\overset{|}{C}}}}-R \xrightarrow{H^+}$$



$$R_1(R)C=O$$

6. Reaction with alkenes

$CH_2=CH_2 + R-Li \rightarrow R-CH_2-CH_2-Li$

7. Electrophilic displacement reaction

$R-X + R'-Li \rightarrow R-Li + R'-X$

8. Nucleophilic displacement reaction

$R-X + R'-Li \rightarrow \cancel{R'-Li + R'-X}\ R-R' + LiX$

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Chemical Kinetics. Unit V

Factors affecting the rate / velocity of a reaction

1. Concentration

The rate of reactions are directly proportional to the concentrations of the reacting species.

2. Temperature

The rates of a reactions are very much affected by temperature a rise of 10 degrees in temperature usually doubles the reaction rate.

3. Catalyst :

positive catalyst increase the rate and negative catalyst decrease the rate of reaction

The study of reaction rate makes us understand the detailed steps by which the reactants are transformed to the products

Rate laws

Let us Consider a reaction

$$A \rightarrow B$$

If $-dc$ is the decrease in the Concentration of A in a time dt and if the molecular concentration of A is c, then,

$$\frac{-dc}{dt} \propto c \quad \text{ie,} = \frac{-dc}{dt} Kc \quad — ①$$

when k is a Constant called velocity Constant or specific reaction rate

For a reaction $2A \rightarrow$ products

$$\frac{-dc}{dt} = Kc^2 \quad — ②$$

and for a reaction $A+B \rightarrow$ Products

$$\frac{-dc}{dt} = Kc_A \cdot c_B \quad \rightarrow ③$$

An Equations which relats the rate of reaction to the Concentration of the reactant is called the rate law or rate equation. Equation (1) (2) and (3) are some of the rate equations or the rate laws.

Rate constant

The rate constant of K of a reactant is defined as the change in concentration of reactants or product per unit time in a reaction in which all the reactants are at unit concentration

Order of reactions

The minimum number of Molecular or atoms of reactants whose concentration determine the velocity of a reaction is called the order of the reaction. It is also defined as the sum of the powers of the concentration terms that occur in the rate equation

$$2H_2O_2 \Longrightarrow 2H_2O + O_2$$

Molecularity of reaction

Definition

The molecularity of a reaction is defined as the minimum number of molecular or atoms of the reactants necessary for the reaction to take place

$$O_3 \rightarrow O_2 + O$$

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Zero Order reactions

Zero Order reaction is one in which the rate of the chemical reaction is entirely independent of the Concentration of the reactant

Differential form of rate equation : $\frac{dx}{dt} = k$

Integral form of rate equation : $k = x/t$

Derivation

Let us consider the Reaction

$A \rightarrow B$

Let 'a' be the initial concentration of A and x be the amount reacted in a time t.

now the reaction

$\frac{dx}{dt} = k$; $dx = kdt$.

on integration : $\int dx = \int k dt$

$x = kt + c$ — ④

where c is the integration Constant. The Value of c is evaluated as follows : At the begining of the reaction t = 0, x = 0

So $0 = k \times 0 - c$ or $c = 0$

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Substituting the Value of c in equation ④

we get $x = kt$ (or) $k = x/t$ — ⑤

This equation ⑤ is known as the Zero Order rate equation, k is the rate Constant

Unit k: $k = x/t = \frac{\text{mole/liter}}{\text{sec}}$

$= \text{mole / litre}^{-1} \text{sec}^{-1}$

ex

photochemical reaction between hydrogen and chloride to form hydrogen chloride

$H_2 + Cl_2 \rightarrow 2HCl$

Thermal decomposition of HI on a gold Surface

$H_2 + I_2 \rightarrow 2HI$

Some enzyme catalysed reactions

Characteristics :

The rate of the reaction does not depend on any concentration term. i.e, the Concentrated of the reactants do not change with time

The Sum of the powers of the Concentration terms that occur in the rate equation is Zero

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First order reactions

First order reaction is one which rate of the chemical reaction depends on one concentration term only. In other words a first order reaction is one in which the reaction is proportional to the concentration of the reactant

Differential form of rate equation

$$dx/dt = k(a-x)$$

Integral form of rate equation

$$k = [2.303/t]\{\log[a/(a-x)]\}$$

Derivation

Let us consider a reaction

$$A \rightarrow \text{products}$$

The rate of the reactions $\frac{-d[A]}{dt}$ $k[A]$

let the initial concentration of A be 'a' moles per litre. If after time 't' x moles per litre of A have decomposed, the remaining concentration of A is (a-x) moles per litre

$$\text{Now } \frac{-d(a-x)}{dt} = k(a-x)$$

$$\frac{dx}{dt} = \left[k(a-x) \text{ since } \frac{-d(a-x)}{dt} = \frac{dx}{dt}\right]$$

$$\frac{dx}{(a-x)} = Kdt \cdot$$

Integrate the above equation

$$\int \frac{dx}{(a-x)} = \int Kdt$$

where C is the integration Constant

The Value of c is evaluated as follows; At the beginning of reaction t=0 and the amount of the Substance reacted x=0, Substituting the Values of x and t in equation (6) we get.

$$-\text{In}(a-0) = k\times 0 + c (\text{or}) \; c = -\text{In}\, a$$

The Value of the rate constant does not depend upon the Unit in which Concentration is expressed.

$$-\text{In}(a-x) = kt - \text{In} \; ; \; kt - \text{In}\, a = -\text{In}(a-x)$$

$$kt = \text{In}\, a - \text{In}(a-x) = \text{In}\frac{a}{a-x}$$

$$k = \frac{1}{t} \; \text{In}\frac{a}{(a-x)}$$

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

The equation (7) is shown as the first order rate equation. K is the rate Constant

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Unit for K : $K = \frac{2.303}{t} \log \frac{a}{a-x}$

$$= \frac{1}{Sec} \frac{Mole/litre}{mole/litre} = sec^{-1}$$

The Value of the rate Constant does not depend upon the Unit in which Concentration is expressed.

Example

Hydrolysis of methyl acetate in presence of acids.

Inversion of cane Sugar in presence of acids.

Characteristics

The rate of the reaction depends of one Concentration term only

the rate of the reaction is proportional to the Concentration of the reactant.

Second order reaction

Second order reaction is depends on two concentration terms. The second order reaction is the rate of two reaction is proportional to squre of the concentration of one substance to the products of the concentration of two substance

$2A \rightarrow$ products

$A+B \rightarrow$ products

Differential form of rate equation for two reactants of equimolor concentration.

$$\frac{dx}{dt} = k(a-x)^2$$

Integral form of rate equation for two reactant of equimolar concentration

$$k = \frac{1}{t} = \frac{x}{a(a-x)}$$

Derivation

$A+B \longrightarrow C+D$

Let us start with equimolar concentration of A and B say "a" moles per litre. Let 'x' moles per litre of A and 'x' moles per litre of B react in a time t. Now the concentration of A will be (a-x) and that of B also will be (a-x)

$$\frac{dx}{dt} = K(a-x)(a-x) = K(a-x)^2$$

$$\frac{dx}{(a-x)^2} = K\,dt$$

on integration

$$\int \frac{dx}{(a-x)^2} = \int K\,dt$$

$$\text{i.e. } \frac{1}{a-x} = Kt + c$$

where c is integration Constant

The Value of c is evaluated as follows. At the beginning of the reaction. The time $t=0$ and the amount of the Substance reacted $x=0$.

Substituting values of x and t in above equation we get

$$\frac{1}{(a-0)} = K \times 0 + c$$

$$c = \frac{1}{a}$$

$$\frac{1}{(a-x)} = Kt + \frac{1}{a}$$

$$Kt + \frac{1}{a} = \frac{1}{(a-x)}$$

$$Kt = \frac{1}{(a-x)} - \frac{1}{a} = \frac{a-(a-x)}{a(a-x)}$$

So,

$$K = \frac{1}{t}\,\frac{x}{a(a-x)} \quad \text{———} \ ⑩$$

The equation (10) is known as the second order rate equation k is the rate constant

ii) Let us consider a reaction

$$2A \longrightarrow \text{product}$$

Let the concentration of A be a mole per liter

Let x moles per litre react in a time t.

Now the Concentration of A will be (a-x)

So

$$\frac{dx}{dt} = k(a-x)^2$$

Rest of the derivation is the same as in a(i) above

Unit for K : $K = \frac{1}{t}\frac{x}{a(a-x)}$

$$= \frac{1}{\text{sec}} \frac{\text{Mole/litre}}{(\text{Mole/litre})(\text{mole/litre})}$$

$$\boxed{K = \text{litre mole}^{-1}\,\text{sec}^{-1}}$$

The Value of rate constant depends upon the Unit in which the Concentration is expressed

$$\frac{dx}{dt} = k(a-x)(b-x)$$ (Differential form of rate equation)

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$ (Integral form of rate equation)

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Third Order reaction:

Third Order reaction is repends on the three Concentration terms. The third Order reaction is the rate of the reaction is proportional to the cube of the Concentration of one substance.

3A → products.

2A + B → products

A+B+C → products

The integral form of reate equations for the three reactants of the same Concentration

$$K = \frac{1}{2t}\left\{\frac{1}{(a-x)^2} - \frac{1}{a^2}\right\}$$

These equation is called Third order equation

$(a-b)^2 = a^2 - 2ab + b^2$

K - Rate Constants

This equation simplification

$$K = \frac{1}{2t}\,\frac{x(2a-x)}{a^2(a-x)^2}$$

$$\text{Unit} = \frac{1}{\text{Sec}}\,\frac{\text{Mole}/\cancel{\text{litre}}\ \text{mole}/\text{litre}}{(\text{mole}/\cancel{\text{liter}})^2\,(\text{Mole}/\text{litre})^2}$$

$$= \frac{1}{\text{Sec}}\ \text{mole}/\text{litre}\ \ \text{mole}/\text{litre}$$

$$= \frac{1}{Sec} \text{ mole}^{-2} \text{ litre}^{-2}$$

$$K = Sec^{-1} \text{ mole}^{-2} \text{ litre}^{-2}$$

Examples

$2NO + Cl_2 \rightarrow 2NOCl$

$2NO + Br_2 \rightarrow 2NOBr$

$2NO + O_2 \rightarrow 2NO_2$

Experssion of half life period of Fst order, 2nd order. and Zero Order reaction

It is donoted $t_{1/2}$

$$x = \frac{a}{2}$$

Sub. first order reaction

$$k = \left[\frac{2.303}{t} \log \frac{a}{a-x}\right]$$

we get

$$K = \frac{2.303}{t} \log \frac{a}{[a - a/2]}$$

$$\log \frac{a}{a/2} = \log \cancel{a} \times \frac{2}{\cancel{a}}$$

$$t_{1/2} = \frac{2.303}{K} \log \frac{a}{a/2}$$

$$= \frac{2.303}{K} \log 2$$

$$= \frac{2.303}{K} \times 0.3010$$

$$\boxed{t_{1/2} = \frac{0.693}{K}}$$

The Half period Of the first order reaction is constant

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Experssion for Half life period of Second order Reaction

$t_{1/2}$; $x = a/2$

Sub 2nd order reaction

$$K = \left[\frac{1}{t} \frac{x}{a(a-x)}\right]$$

we get

$$K = \frac{1}{t_{1/2}} \frac{a/2}{a-(a-a/2)}$$

$$t_{1/2} = \frac{1}{k} \frac{\cancel{a/2}}{a\,\cancel{a/2}}$$

$$= \frac{1}{Ka}$$

$$\boxed{t_{1/2} \propto \frac{1}{a}}$$

The half life period of the Second order reaction is inversely proportional to the concentration of the reactant.

Experssion for the Half period of third order reactions

$t_{1/2}$; $x = a/2$

Sub 3rd order Rnx

$$k = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$$

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$$K = \frac{1}{2t_{1/2}} \left[\frac{1}{(a - a/2)^2} - \frac{1}{a^2} \right]$$

$$K = \frac{1}{2t_{1/2}} \left[\frac{1}{\left(\frac{a}{2}\right)^2} - \frac{1}{a^2} \right]$$

$$t_{1/2} = \frac{1}{2K} \left\{ \frac{4-1}{a^2} \right]$$

$$t_{1/2} = \frac{3}{2Ka^2} \qquad \frac{3}{2K} = \text{Constant}$$

$$\boxed{t_{1/2} \propto \frac{1}{a^2}}$$

The half life period of the third order reaction is inversely proportional to the concentration of the reactant.

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Expression for the half like period of Zero Order Reaction

$t_{1/2}$; $x = a/2$

Sub Zero order rate Equation

$$K = \frac{x}{t}$$

$$= \frac{a/2}{t_{1/2}}$$

$\frac{1}{2} K$ = Constant.

$$t_{1/2} = a/2K$$

$$\boxed{t_{1/2} \propto a}$$

The half life period the Zero order reaction is directly proportional to initial Concentration

X Pseudo First Order reaction

The reaction whose molecularly is two But order is one is called pseudo first order reaction

Explanation

Consider the reactions

$$A + B \rightarrow C$$

The above reactions to takes place one molecule of A and one

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Molecule B are essential so it is molecularity is two

Let us double the concentration of A keeping B Constant. So the rate of the reaction is doubled. So the reaction is bimolecular and Second order.

The molecularity of a reaction is two But order is only one. So the reaction is known as pseudo first Order Reaction

Example

Hydrolysis of ethyl acetate in Water

$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$

Methodes for determination of Order of reaction

Method 1:

1. Integration Method [Hit and trial Method]

* Using characteristic equation

In this methode the ~~ob~~. initial Concentration of all the reactants taking part of determind.

The Concentration of the reacting Substance at different intervels of time are also determind

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The Different Values of x are determind.

These Values are substituted in the different rate equation.

The equation which gives the most constant Values of Volacity Constant for a Serious of interval of time will give Order of the reaction

Limitations :

* This method can't be Use Complex reactions

* In this method should be studied time, interval of the reactions.

2. Differential Method.

We know that $\frac{dx}{dt} = K(a-x)^n$

Taking log on both sides

$$\log\left(\frac{dx}{dt}\right) = \log k + n\log(a-x)$$

A graph drawn $\log\left(\frac{dx}{dt}\right)$ vs $\log(a-x)$

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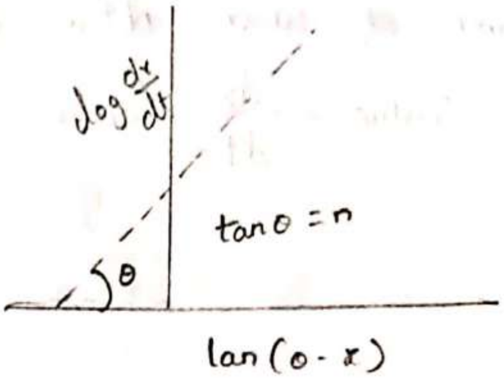

The slope of ~~C~~ curve is found the slope gives the order of the reactions

3. Graphical Method.

First Order reactions

$$\frac{dx}{dt} = K(a-x)^1$$

Second order reaction

$$\frac{dx}{dt} = K(a-x)^2$$

Third order reactions

$$\frac{dx}{dt} = K(a-x)^3$$

n^{th} Order reactions

$$\frac{dx}{dt} = K(a-x)^n$$

To find $\frac{dx}{dt}$

The Values of dx/dt at a different intervels of time Can be determind by ~~Plotting~~ plotting a curve between x and time t.

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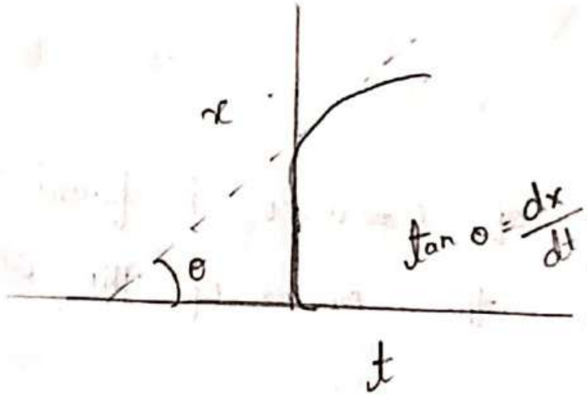
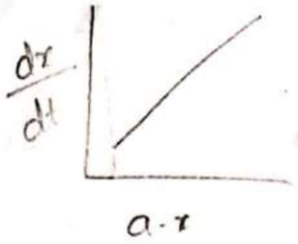
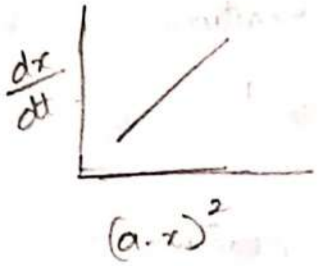
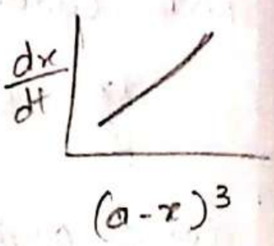
The Nature of curve obtain the figure the slope Value = $\frac{dx}{dt}$



The slope is nothing that tan θ Value.







4. Half life method :

we have already ~~di~~. half life reactions is independent of Concentration for a first order Reaction

It is inversely proportional to the Concentration Second Order Reaction

It is inversely proportional to the Square of the Concentration for a third Order Reaction

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The half life change in any order is inversely proportional to the initial Concentration Reaction to the power

$$t_{1/2} = \frac{K}{a^{n-1}}$$

where,

n - Order of Reaction

t_1, t_2 - The time intervals for half change of particular Reaction

$$t_1/t_2 = \left[\frac{a_2}{a_1}\right]^{n-1}$$

a_2, a_1 = Initial Concentration

The Order of the Reaction Can be Calculated above Equation

Ostwalds isolation

The Reating Substance a taken in large excess, it Concentration does not change

It Can be taken as Constant

All, Reaction is except one are taken is large excess and the Order of Reaction is determination by this Method. The process Reaction of the Reaction Some, the of the all the total of order of Reaction

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Adventage

* Each Component Can be differented Separatly
* This are the Method of Order of Reaction

principle are techniques of kinectic Reaction

Principle :

The change in Some properties of Reaction or products are Measured at Various intervals of time, and from the Rate Constant Cannot be calculated

~~Teckiq~~ Techniques

volumetry :

In the techniques, the change in Volum of Reactants and products

Kinetics of decomposition of H_2O_2 :

This can be studied by the techniqous in the presence of platinum block.

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H_2O_2 decomposes into water and oxygen

The reaction can be followed in two water by cooling the Oxygen, gas evolved during the decomposition and Measuring its Volume at definite intervals of time

Let V_t - Volume of oxygen, evolved at time t

$$t = V_\alpha$$

The amount Reacted after the time

$t = x = V_t$

Concentration be the Volume at the end of the Reaction, then the initial Concentration after time $t = (a - x) = V_\alpha - V_t$.

$$K = \frac{2.303}{t} \log \frac{V_0}{V_\alpha - V_t}$$

The equal position of H_2O_2 are titrated

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Comparision between CT and ARRT :

In the Collision theory of Reaction Rates the Frequency Factor A is found to be Related to the number of collisions talking place per Unit Volume per second . Z In the Activated Complex theory the Frequency Factor is Found to be Related to the Entropy of Activation

In the Case of a Reaction Involving Simple Molecules , that is Molecules which Can be taken as Rigid Spheres, the two theories agrees. That is, the Value of A Calculated from Equation (14) has been found to be Same as the Value of Z.

In the Case of Reactions Involving Complex Molecules ; the Collision theory fails ; But still the absolute Reaction Rate theory holds good because the Experimental Value agrees with the Calculated Values from Equation Therefore the absolute Reaction Rate theory is Saperior to the collision theory.

Reason for the failure of collision theory:

When we Consider Complex Molecules, they Contain large Number of atoms. When they form Activated Complex there is a large decrease in the entropy. From Equation we know that

$$A = \frac{KT}{h} e^{\Delta S^* / R}$$

The Value KT/h is always Constant. So when there is decrease in the Value of entropy the Value of A decreases Considerably. Therefore for Complex Reactions, the Value of the Frequency Factor is less when Compared to Simple Molecules for which it is equal to 1. Therefore it becomes necessary to introduce to probability factor p in the Equation for the collision theory of Reaction Rates. A is Related to PZ

Principle are techniques of kinetic reaction:

principle:

The change in Some properties of reaction or products are measured at various intervals of time, and from the rate constant cannot be calculated.

Techniques:

Volumetry:

In the techniques, the change in volum of reactants and products.

kinetics of decomposition of H_2O_2:

This can be studied by the [illegible] in the presence of platinum block.

H_2O_2 decomposes into water and oxygen:

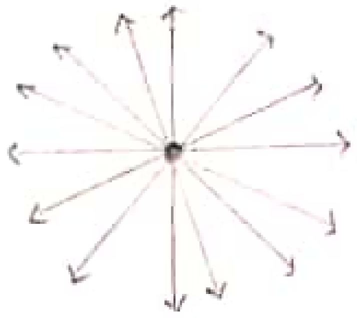
The reaction can be fallowed in two water by cooling the oxygen, gas evolued, during the decomposition and measuring its volume at definite intervals of time.

The relationship between the various factors is given by the following equation.

$$[\alpha]_D^t = \frac{\alpha}{lc}$$

Where $[\alpha]_D^t$ is the specific rotation for sodium D line at $t°c$, a = optical rotation ; l = length of the cell in dm and c = concentration of the solution in g/cc.

The specific rotation is measured by an instrument called polarimeter. Study of reactions using a polarimeter is called polarimetery.



when ordinary, non-polarised light is passed through a nicol prism it becomes plane polarised ie., the electric and magnetic vectors vibrate in only one direction

when this polarised light is passed through some substances, the plane of the plane polarised light is turned either to the left or right. Such substances are called optically active. The phenomenon is called optical activity

The optical rotation arising because of optical activity of substances can be used to follow the kinetics or reactions.

The optical rotation depends on.

I. The wavelength of the light, λ.

ii) Temperature, T

iii) The cell length, l and

iv) The concentration of the solution, c

Manometry:

principle:

using a manometer the pressure of a reaction mixture can be measured at different intervals of time From the pressures measured at different intervals of time the rate constant can be calculated. This technique can be applied only if both the reactants and products are gases.

Experiments:

Tertiary butyl peroxide decomposes to give acetone and ethane.

$$\underset{\text{t - butyl peroxide}}{(CH_3)_3C-O-O-C(CH_3)_3} \longrightarrow \underset{\text{acetone.}}{2CH_3-CO-CH_3} + CH_3-CH_3$$

The above reaction is conducted in vapour state. The initial pressure of the reactant is measured as P_0. one mole of t-butyl peroxide decomposis to give two mole of acetone and one mole of ethane. That is the pressure is increased three times. The final pressure of the product is $3P_0$. That is $3P_0 - P_0 = 2P_0$ The value of $2P_0$ is directly proportional to the initial concentration of the peroxide.

Let V_t = Volume of oxygen, evolved at time t

$t = V_\alpha$

The amount reacted after the time

$t = x = V_t$

concentration be the volume at the end of

the reaction, then the initial concentration after

time $t = (a-x) = V_\alpha - V_t$

$$k = \frac{2.303}{t} \log \frac{V_0}{V_\alpha - V_t}$$

The equal portion of H_2O_2 are titrated against standard $KMnO_4$. Solution at regular intervals.

The titrated value gives amount of H_2O_2 and decomposed.

This method is more covenient

The experimental result shows that decomposition of H_2O_2 follows first order kinetics.

Calculation:

The volume of $KMnO_4$ required by a particular volume of hydrge peroxide (H_2O_2) The beginning of experiment equal to $V_1 \alpha$

The initial concentration of $H_2O_2 = a$.

The volume of $KMnO_4$ required by some volume of H_2O_2 after a time intervals $t = t_2 \alpha$.

The concentration of H_2O_2 remaining at the time $t = a-x$.

The values of 'a' and 'a-x' are substituted first order rate equation.

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$k = \frac{2.303}{t} \log \frac{V_1}{V_2}$$

This value k is found to be constant showing that decomposition of H_2O_2 follows 'First order reaction'