Model Answer (1st Semester-2018)

Subject - Chemistry.

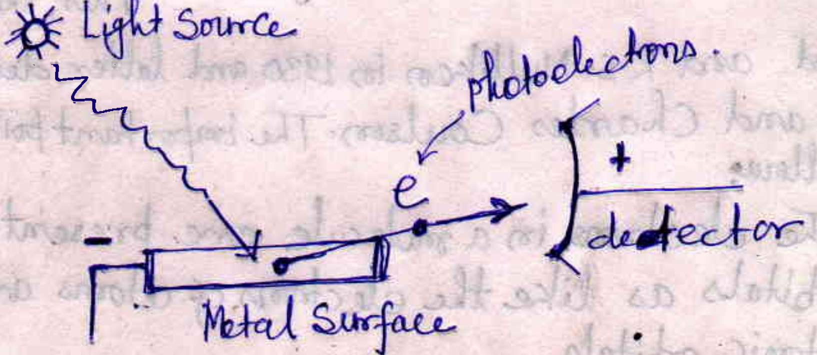
Q. 1. Ans:-

(i) → ⓑ
(ii) → ⓑ
(iii) → ⓒ
(iv) → ⓑ
(v) → ⓑ
(vi) → ⓑ
(vii) → ⓐ

Fill in the blanks :-

(vii) → CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4.
(IX) → As metamers.
(X) → Functional group isomers.

Q. 2. (i) Ans:- Photoelectric effect:- When a beam of light falls on the certain metals (like K, Rb, Cs etc) the electrons are ejected from the metals. Such electrons are known as photoelectrons and phenomenon is known as photoelectric effect.



(ii) Results of Photoelectric effect:-

ⓐ When the beam of light strikes the metal surfaces the electrons are ejected immediately. There is no time lag between the striking of light beam and the ejection of photoelectrons.

ⓑ The number of electrons ejected is proportional to the intensity of Light.

(P.T.O)

Q.2(ii)

ⓒ There is a characteristics minimum frequency ν_0 (also known as threshold frequency) below which photoelectric effect is not possible.

ⓓ The K.E. of these electrons increases with the increase of frequency of the light used.

By using this results Einstein (1905) also explain the photoelectric effect with help of planck's quantum theory. That is,

$$E = W_0 + \frac{1}{2} m_e v^2$$

$$\Rightarrow E = W_0 + K.E$$

$$\Rightarrow \boxed{h\nu = h\nu_0 + \frac{1}{2} m_e v^2} \text{ ——— ⓘ}$$

where

h = placks Constant $(h = 6.626 \times 10^{-34}\ \text{JS})$

ν = frequency of radiation fall

ν_0 = threshold frequency

m_e = mass of electrons $(m_e = 9.1 \times 10^{-31}\ \text{kg})$

V = velocity of photoelectrons.

Q3. Ans -(i) Molecular orbital Theory (MOT):-

This theory was developed by F. Hund and R.S. Mulliken in 1930 and latter develped by I.E. Lennard-Jones and Charles Coulson. The important points of this theory are given as follow;

(a). The electrons in a molecule are present in the various molecular orbitals as like the electrons of atoms are present in the various atomic orbitals

(b) The atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.

(c). An electron in the atomic orbital is influenced by one nucleus, in a molecular orbital it is influenced by two or more nuclei.

Hith

Q.3.(i) Ans:-

ⓓ. The atomic orbitals are monocentric while a molecular orbital is polycentric.

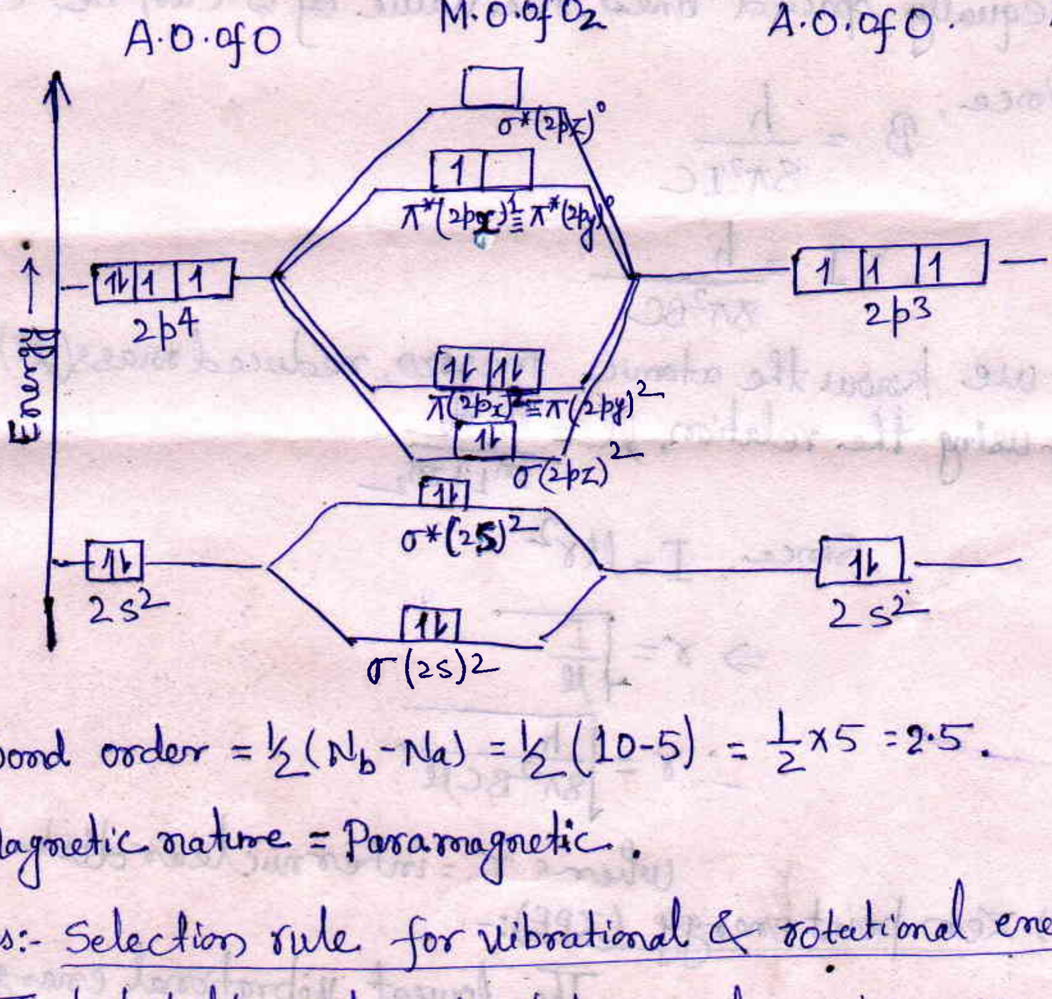
ⓔ. When two atomic orbitals combine, two molecular orbitals are formed, one is known as bonding M.O. while the other is known as antibonding M.O.

ⓕ. The bonding M.O has lower energy and hence greater stability than the corresponding antibonding M.O.

ⓖ. The M.Os. like atomic orbitals are filled accordance with the aufbau Principle, Paulis exclusion Principle and Hunds rule.

(ii) Ans:- M.O. diagram of O_2^+ :-

$O_2^+ : KK' \sigma(2s)^2, \sigma^*(2s)^2, \sigma(2p_z)^2, \pi(2p_x)^2 \equiv \pi(2p_y)^2, \pi^*(2p_x)^1 \equiv \pi^*(2p_y)^0$.



Bond order $= \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10-5) = \frac{1}{2} \times 5 = 2.5$.

Magnetic nature = Paramagnetic.

Q.4. (i) Ans:- Selection rule for vibrational & rotational energy levels:

The probability of transition between two given energy levels is determined by selection rules. A selection rule specify the changes in the quantum number accompanying a particular transition. Selection rule are obtained from the quantum theory of interaction of radiation with matter and backbone of spectroscopy.

For rotational level selection rule is;

$$\Delta J = \pm 1$$

Where J is rotational quantum numb

and for vibrational level selection rule is;

$$\Delta V = \pm 1$$

where V is vibrational quantum number

Meaning there by if the transition follow the selection rule, it is allowed transition and having more intense spectral line obtained while the transition not follow the selection rule it is forbidden transition and having less intense spectral line.

Q.4.(ii) Bond Length from Rotational Spectrum:-

From the rotational spectrum, which consists of series of equally spaced lines, the value of 'B' can be calculated.

Since, $B = \frac{h}{8\pi^2 IC}$

$$\therefore I = \frac{h}{8\pi^2 BC}$$

If we know the atomic masses, reduced mass (μ) can be calcula by using the relation, $\mu = \frac{m_1 m_2}{m_1 + m_2}$

Since, $I = \mu r^2$

$$\Rightarrow r = \sqrt{\frac{I}{\mu}}$$

$$\therefore r = \sqrt{\frac{h}{8\pi^2 BC\mu}}$$

where r = internuclear distance or bond leng

Q.5.(i) Zero point energy (ZPE):-

The lowest vibrational energy level whic is not equal to zero but it is equal to $\frac{1}{2}h\nu$. This is known as zero point energy. In other words, the zero point energy is just half of the energy difference between two nearest vibrational energy levels, i.e. the quantity $\frac{1}{2}h\nu$ i known as the zero point energy. It depends only on the classical vibrational frequency. The ZPE means that the atoms in a molecule ca never be completely at rest relative to each other. This fact is approval of

Q.5.(ii) Ans:- Energy level diagram for various molecular energy from vibrational and rotational levels;

According to Born-oppenheimer approximation the total energy of molecule is,

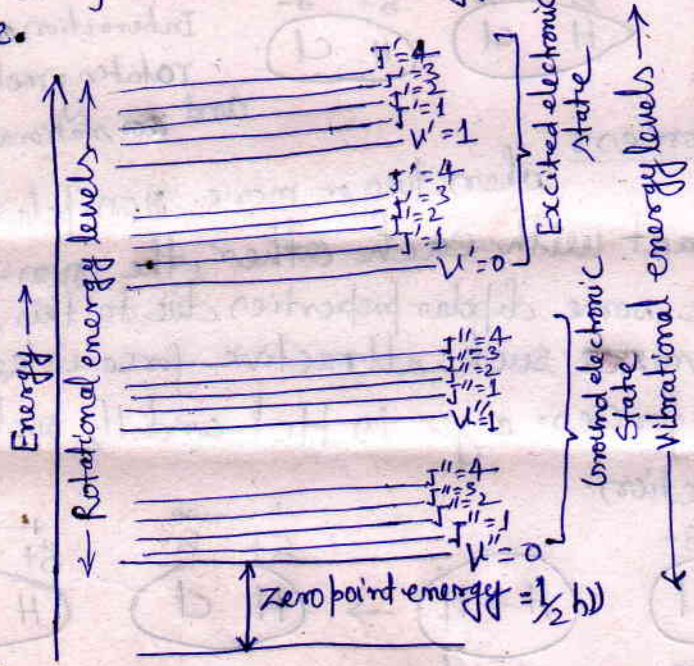
$$E = E_{el} + E_{vib} + E_{rot} + E_{tr}.$$

More over, $E_{el} > E_{vib} > E_{rot.} > E_{tr.}$

So, the translation energy is very small, we write the Born-Oppenheimer approximation as;

$$E = E_{el} + E_{vib} + E_{rot}.$$

It is to be important that a series of rotational energy levels (designated by the rotational quantum number J) are associated with each vibrational energy level (designated by the vibrational quantum number V). And a series of vibrational energy levels are associated with each electronic state.



where,

J'' = Rotational quantum number for ground electronic state

J' = Rotational quantum number of excited electronic state

V'' = vibrational quantum number for ground electronic state

V' = vibrational quantum number for excited electronic state.

Q.6. Sol:- Given, $r = 1.13 A^\circ = 1.13 \times 10^{-10} m$, $\mu = \frac{m_1 m_2}{m_1+m_2} = \frac{(1.99\times10^{-26} kg)(2.66\times10^{-26} kg)}{(1.99+2.66)\times10^{-26} kg}$

$$\mu = 1.14 \times 10^{-26} kg$$

$$I = \mu r^2 = (1.14\times10^{-26} kg)(1.13\times10^{-10} m)^2 = 1.46\times10^{-46} kg\, m^2$$

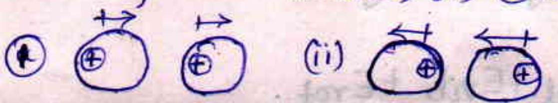
$$E_1 = \frac{\hbar^2}{I} \text{ Joule} = \frac{(1.054\times10^{-34} Js)^2}{(1.46\times10^{-46} kg\, m^2)} = 7.61\times10^{-23} \text{ Joule}$$ Ans.

And, $E_1 = \frac{1}{2} I\omega^2$, where ω is the angular velocity, hence,

$$\omega = \sqrt{\frac{2E_1}{I}} = \sqrt{\frac{2\times(7.61\times10^{-23} J)}{1.46\times10^{-46} kg\, m^2}} = 3.23\times10^{11} \text{ radian } s^{-1}$$ Ans

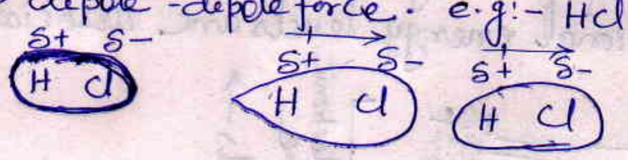
Q.7. (i) Types of van der Waal's forces:- The attractive intermolecular forces are known as van der Waal's forces. It is of three types:

ⓐ Dispersion forces or London forces:- When two or more temporary dipolar molecules comes in contact with each other a attractive force exist between them, such attractive force is known as dispersion force.



Interaction energy $\propto \frac{1}{r^6}$: where 'r' is internuclear dista

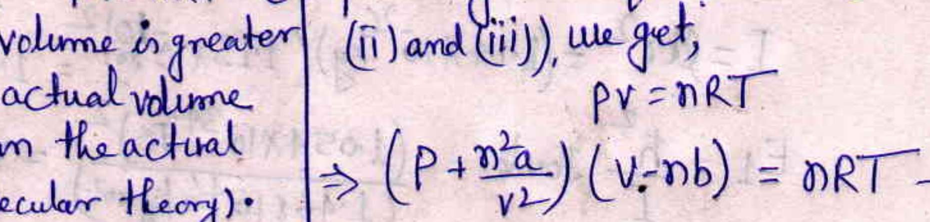
ⓑ Dipole-dipole forces:- When two or more dipolar molecules comes in contact with each other a attractive force exist between them, such attractive force is known as dipole-dipole force. e.g:- HCl molecules:



Interaction energy of rotating molecule $\propto \frac{1}{r^6}$ and stationary molecule $\propto \frac{1}{r^3}$

ⓒ Dipole-induced dipole forces: When two or more non-polar and dipolar molecules comes in contact with each other, the non-polar molecules also experience some dipolar properties due to this, a attractive force exist between them such attractive force is known as dipole-induced dipole forces. e.g:- in HCl and H_2 molecules shown such types of attraction.

Interaction energy $\propto \frac{1}{r^6}$



(ii) Vander Waal's equation (or Real gas equation):-

From ideal gas equation, $PV = nRT$ —(i)

In ideal gas equation, the volume is greater than the actual volume and pressure is ~~less~~ than the actual pressure (from kinetic molecular theory).

Both the terms are required for correction.

Volume correction (V) $= V - nb$ —(ii)

and pressure correction (P) $= \left(P + \frac{n^2a}{v^2}\right)$ —(iii)

where 'a' and 'b' are vander Waal's Constant.

Both the correction terms are –

putting in equation (i) (i.e. from eq^{n}s (ii) and (iii)), we get,

$PV = nRT$

$\Rightarrow \left(P + \frac{n^2a}{v^2}\right)(V - nb) = nRT$ —(iv)

The equation (iv) is known as vander Waal's equation or equation of state for real gas.

* **

Q. 1 ⓐ What do you mean by the term chirality? Illustrate with simple example.

Ans → Anything which is non-superimposable on its mirror image form is called chiral. The phenomenon of superimposition is done by ~~stop~~ picking the compound and ~~stop~~ covering on its mirror image form; ~~but~~ the plane of the compound / molecule shall remain the same.

Non-superimposable molecules are optically active i.e the molecules turn / rotate the plane polarized light in either left hand side or right hand side.

Examples: Z, Q, $CH_3 \cdot \overset{*}{C}H(OH) \cdot COOH$ etc.

ⓑ Write the structure of an organic compound, which does not have any asymmetric carbon atom, but optically active.

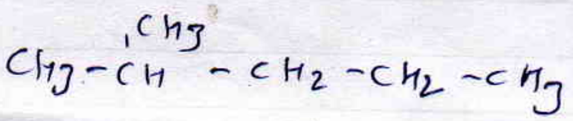
Ans →

P. Kuma

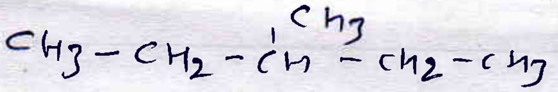
Q.2 ⓐ How many structural isomers are possible for C_6H_{14}, write structures and names also.

Ans →

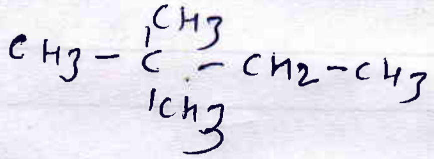
$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$ Hexane



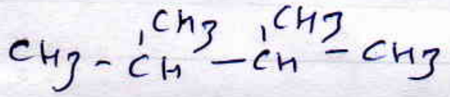
$CH_3-\overset{CH_3}{CH}-CH_2-CH_2-CH_3$ 2-methylpentane



$CH_3-CH_2-\overset{CH_3}{CH}-CH_2-CH_3$ 3-methylpentane



$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_3$ 2,2-dimethylbutane

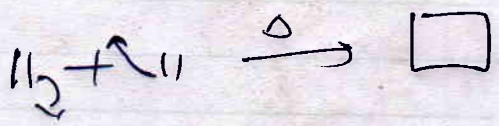


$CH_3-\overset{CH_3}{CH}-\overset{CH_3}{CH}-CH_3$ 2,3-dimethylbutane

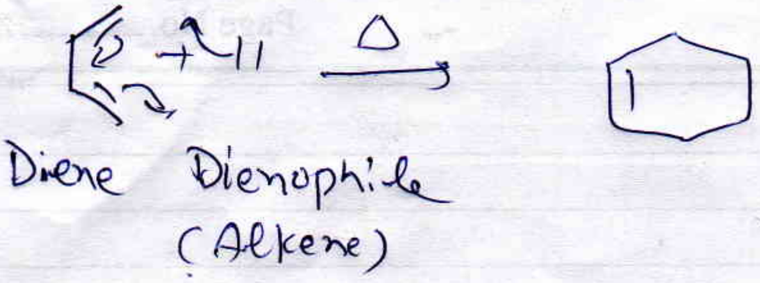
ⓑ Write notes on Diels Alder cyclization reactions i.e. [2+2] and [4+2] cycloaddition reactions

Ans — Diels Alder reaction involves the combination of alkenes or polyenes to form a cyclic compound. These require only Heat for the activation, not the light, No intermediate formation

(i) [2+2] cycloaddition



(ii) [4+2] cycloaddition

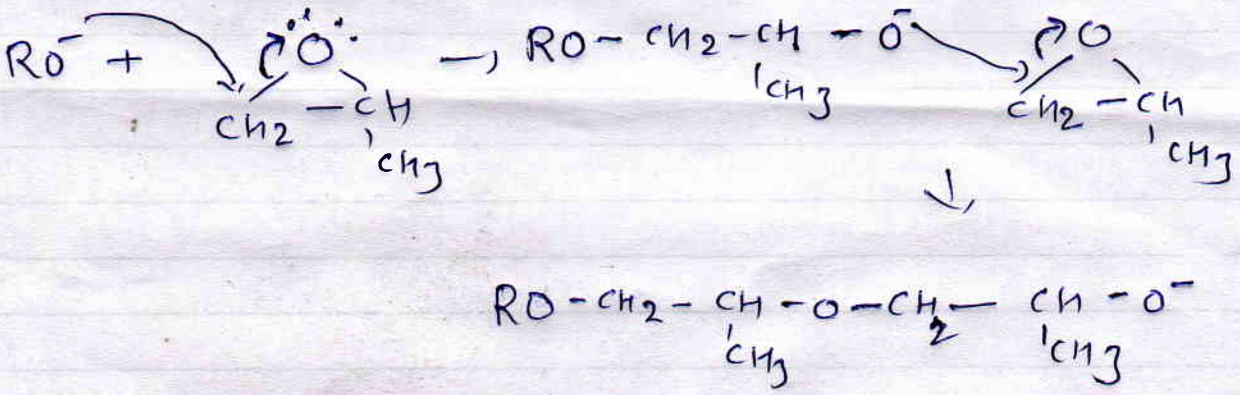


Dienophile - Loves a diene

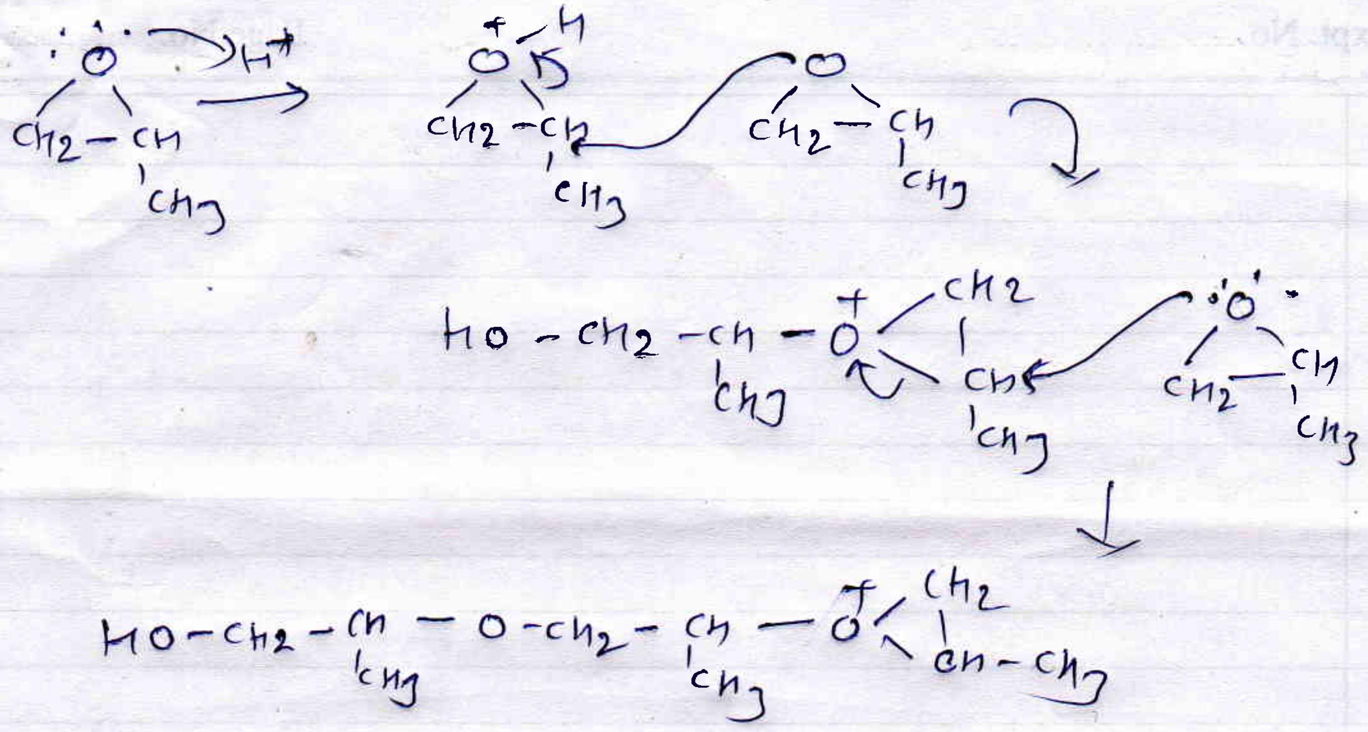
Q.3 (a) write the mechanism of Epoxide ring opening reactions by Cationic and Anionic mechanism.

Ans (i) Anionic mechanism (ie catalysed by a nucleophile)

Such as OH^- or RO^-.

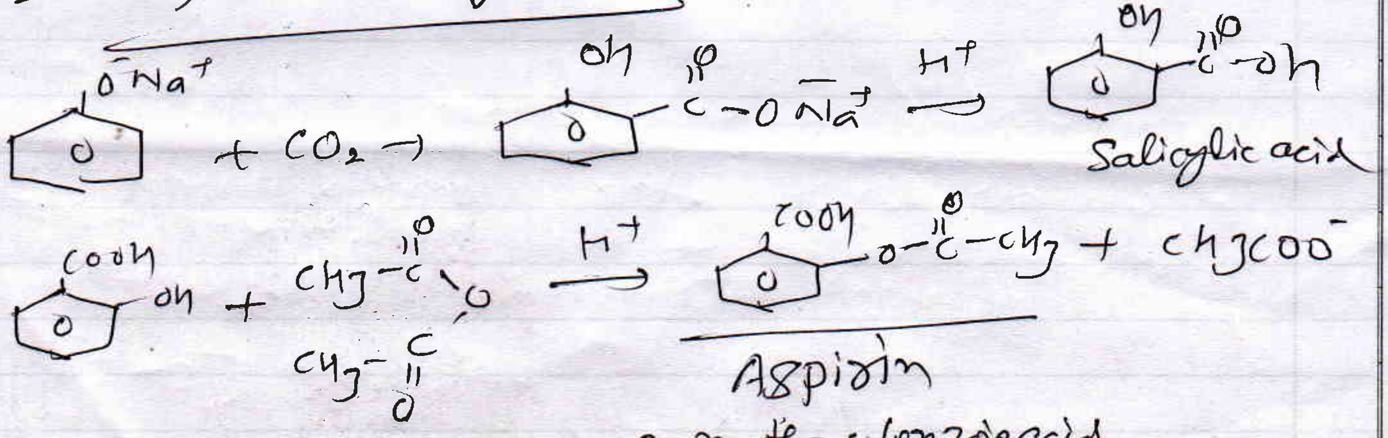


(ii) Cationic mechanism (ie Catalysed by an electrophile)



① Write the reactions of preparation of Aspirin.

Ans By kolbe's synthesis

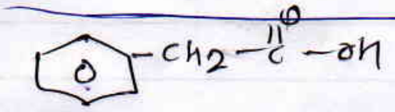
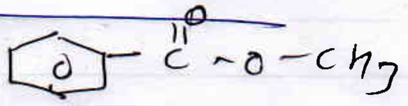


2 - methoxy benzoic acid

Acetyl salicylic acid

Q ① $CH_4 + Cl_2 \xrightarrow{UV} ?$

(ii) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_3$ and $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$ are related as ... isomers.

(iii)  and 

are related as ... isomers

Ans ① $CH_4 + Cl_2 \xrightarrow{UV} CH_3Cl + HCl$

$\downarrow Cl_2, UV$

$CH_2Cl_2 + HCl$

$\swarrow Cl_2, UV$

$CHCl_3 + HCl$

$\swarrow Cl_2, UV$

$CCl_4 + HCl$

(ii) As metamers

(iii) Functional group isomers.

P.Kar