

**II.M.Sc.,CHEMISTRY**  
**ORGANIC CHEMISTRY -III**  
**SEMESTER-III**

**UNITS – 3**

**PHYSICAL METHODS OF STRUCTURAL DETERMINATION**

**PART - 2**

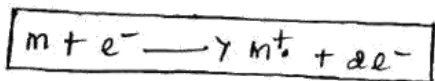
**By,**  
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**ASSOCIATE PROFESER OF CHEMISTRY ,**  
**PERIYAR ARTS COLLEGE,**  
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## 17) Various Ionisation techniques in MS

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### ① Electron Ionisation method :-

- (i) The sample molecule is volatilized in a separate chamber where vapours ~~pressure~~ of molecules at  $10^{-4}$  to  $10^{-5}$  are allowed into ionization chamber.
- (ii) In the ionization chamber, ionization is brought about by bombarding the sample molecules with high energy electrons.
- (iii) The electrons for bombardment are obtained from a heated tungsten or rhenium filament.
- (iv) On the opposite side of the ion source, there is a plate known as electron trap which has an electrical connection to the filament and is held at a positive potential with respect to the filament.
- (v) By means of collimating magnets, the negatively charged electrons are drawn towards the trap and towards the ionization chamber.
- (vi) In the ion source, high energy bombarding electrons produce a field by means of which ionization of molecule occurs. The field produced interacts with electrons of the molecule, resulting in the removal of electrons from the molecule.



- (vii) The accelerated electrons of high energy (70 eV) on impact with molecules produce positive ions along with small amounts of negative ions and neutral particles. The positive ions are selectively pushed out by using electrodes with a small positive charge. The negatively charged

Particles are neutralized by the pusher plate and neutral particles are continuously pumped out. The positive ions are accelerated by electrodes maintained at a high potential (1-10 keV) and then enter the magnetic field which resolves them.

(viii) The time span from formation to ejection of the ions from the ion source is about 1-5  $\mu$ s. ( $10^{-6}$  sec).

## II. Chemical Ionisation:

① In this method, a reagent such as methane, Probutane or ammonia is introduced into a high pressure source (0.1 to 1 torr) and ionized by electron bombardment.

② Primary reagent ions are produced by the following equation



(Primary reagent ions)

③ Secondary reagent ions are produced by collision of primary reagent ion with reagent molecule ( $\text{CH}_4$ ) and produce stable secondary reagent ions.

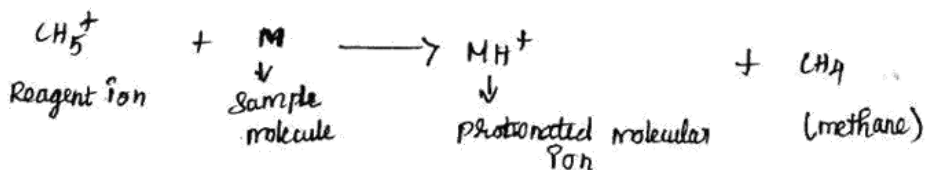
This occurs due to high pressure in the chemical ion source.



④ The above reaction is an acid-base reaction in which  $\text{CH}_4^+$  is acting as proton donor (acid) and  $\text{CH}_4$  is acting as proton acceptor (base).

Again protonation reaction occurs if we introduce a small amount of the sample in the vapour phase into the CI source (CI - chemical ionization)

between the reagent ions  $\text{CH}_5^+$  and sample molecule (M).



MH<sup>+</sup> ion is known as quasimolecular ion which is having 1 amu

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greater than molecular ion.

(6) The transfer of ions between two species depends on proton affinity of the two species.

#### Advantages:-

(i) More abundant peaks related to the molecular ion whether M<sup>+</sup>, M+1 or M-1 are got.

(ii) Similar fragmentation patterns, which make it easier in many cases to study the kinetics of the reaction of individual ions.

(iii) GC-MS - Gas chromatography interfacing with mass spectroscopy can be done in chemical ionization since methane can be used not only as reactant gas in chemical ionisation but also as the carrier gas in gas chromatography.

#### III. Field Ionization and field description:-

(1) An organic compound under investigation in vapour phase can be ionised when it is passed near a sharp metal anode carrying an electric field of the order of  $10^{10}$  V/m.

(2) Electrons are sucked from the organic compounds into the incomplete orbitals of the metal anode. Resulting molecular ions are repelled towards a slit cathode.

(3) Then the ions are focused magnetically and electrostatically is an electron-impact studies.

### Advantages:-

- (i) Molecular ions are abundantly increased and complex fragmentation and rearrangements are minimized. 10
- (ii) outstanding advantage can be achieved by a modification of the technique in which the sample is deposited directly into the anode and the high field produces not only ionisation but also desorption.
- (iii) Unstable and involatile material can be handled in this way.
- (iv) Molecular ion peaks have been produced from complex naturally occurring compounds notably the carbohydrates which do not show  $M^+$  peaks in EI.

### iv Plasma desorption:-

- ① In this desorption method, the sample deposited on a thin foil which is held at high voltage 10-20 kv.
- ② Secondary sample mol. ions are accelerated at this high voltage
- ③ Enormously energetic ions are produced from fission fragments of  $^{252}\text{Cf}$  :  $^{252}\text{Cf}$  produces 3% of various ion pairs. These ion-pairs in turn decompose giving  $^{142}\text{Ba}$  &  $^{106}\text{Te}$ .
- ④ These enormously energetic ions strike the sample molecule in the thin foil and generate about  $10^{12}$  W of power and a localized plasma at a temperature of around 10,000K is produced. So the target molecules ionise at this high temperature.

IV plasma desorption continuation: .

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V. Secondary Ion mass spectroscopy (SIMS):

(i) A beam of Primary Ions are produced from rare gases such as Ar, Xe, Ne etc.

Primary Ion such as  $Ar^+$  is directed to hit on the target molecule.

(ii) Energy of Primary Ions is transferred to the target molecule and the target molecules undergo ionisation. The Ions of target molecules are known as secondary Ions.

VI Fast atom bombardment (FAB):

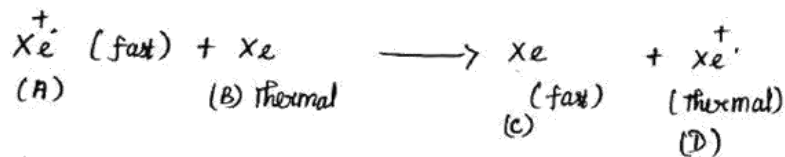
(i) The sample is dissolved in a viscous liquid (generally glycerol). This viscous solution of the sample is coated on a metal plate.

(ii) Ionisation of the sample is achieved by the bombardment of the sample matrix by a beam of fast moving neutral atoms.

(iii) The bombarding neutral atoms are usually rare gases either xenon or argon.

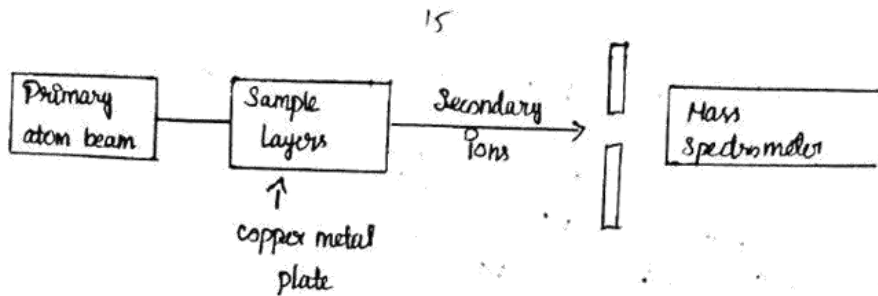
(iv) The atoms of the rare gases are first ionised and these Ions are then passed through an electric field to get accelerated.

(v) After acceleration, the fast moving Ions enter into a chamber containing further rare gas atoms and collision of Ions and rare gas atoms lead to charge exchange as follows.



(vi) The fast atoms Xe (c) now regain the kinetic energy of fast Ion (a) and proceed towards the analysis.

(vii) By means of deflector plate, with a negative potential, the remaining fast Ions (a) and Ions with thermal energies (D) can be removed before the sample bombardment.



### Advantages:-

- (i) FAB can be applied to the ionisation of high molecular weight samples of biological origin and compounds with molecular weights well in excess of 5000 Daltons.
- (ii) FAB has been used to get mass spectra of salts.
- (iii) FAB spectra usually provide relatively abundant molecular or quasimolecular ions and also show some structurally important fragment ions.

### Disadvantages:-

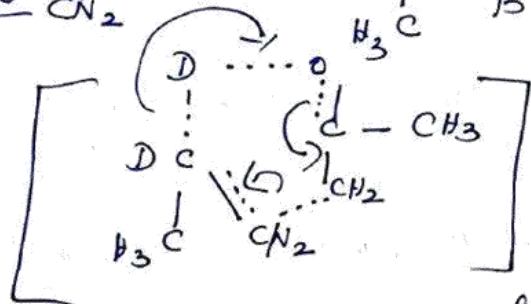
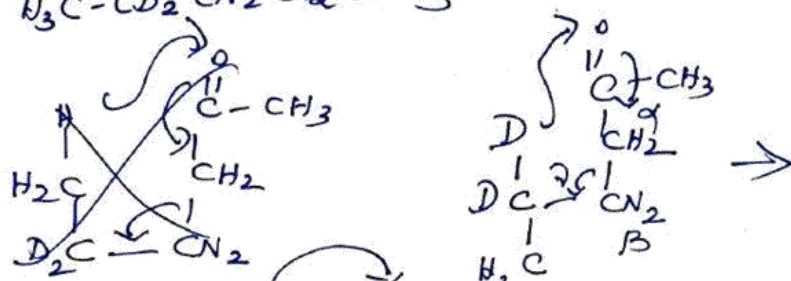
- (i) Matrix also forms ions on bombardment in addition to those formed by the sample this will complicate the spectrum.
- (ii) A major drawback is the problem of quantitative measurement because FAB samples the surface rather than the bulk concentration of the solute present.

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 (14) Explain Mc-Lafferty rearrangement

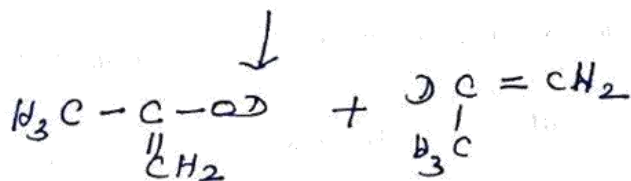
- (i)  $\text{H}_3\text{C}-\text{CD}_2\text{CN}_2\text{CH}_2\text{COCH}_3$
- (ii) Alkyl ethers
- (iii) Aliphatic esters

Defn:- See before

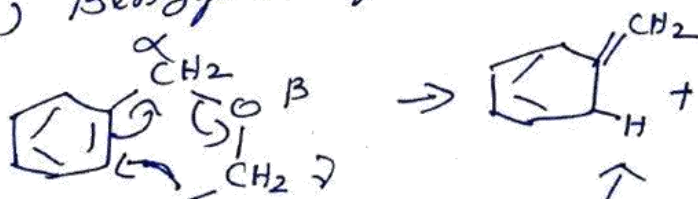
(i)  $\text{H}_3\text{C}-\text{CD}_2\text{CN}_2\text{CH}_2\text{COCH}_3$



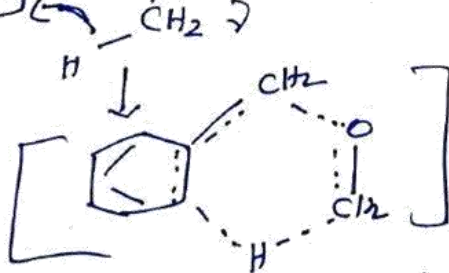
Six-membered cyclic transition state



(ii) Alkyl ethers :-  
 (E.g) Benzyl methyl ether



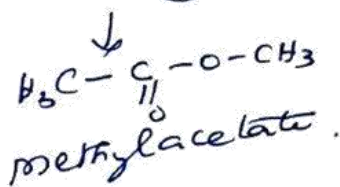
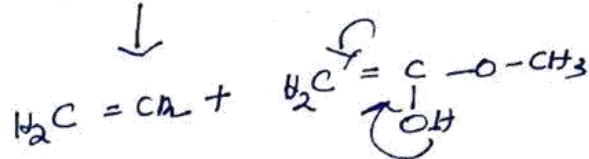
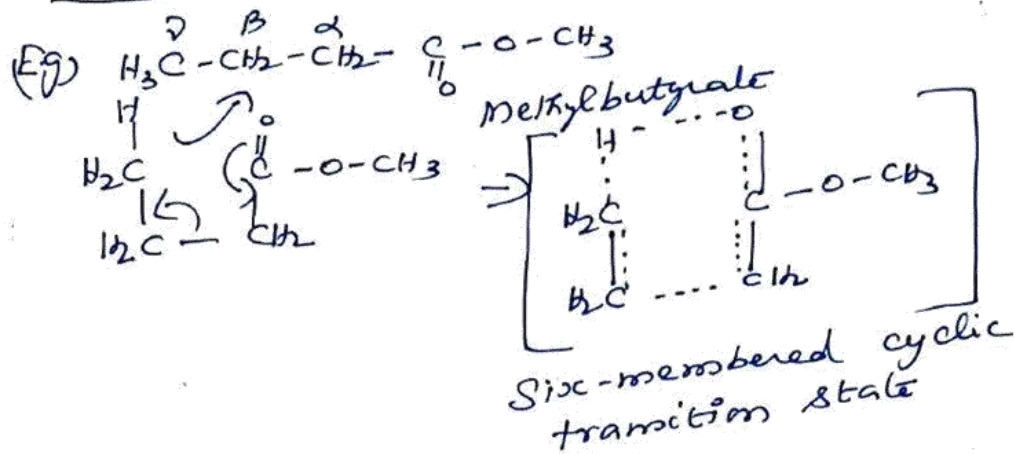
$\text{CH}_2=\text{O}$   
 formaldehyde



Six-membered cyclic transition state.



(iii) Aliphatic ester:-



15) Explain the mass spectra of primary, secondary and tertiary alcohols

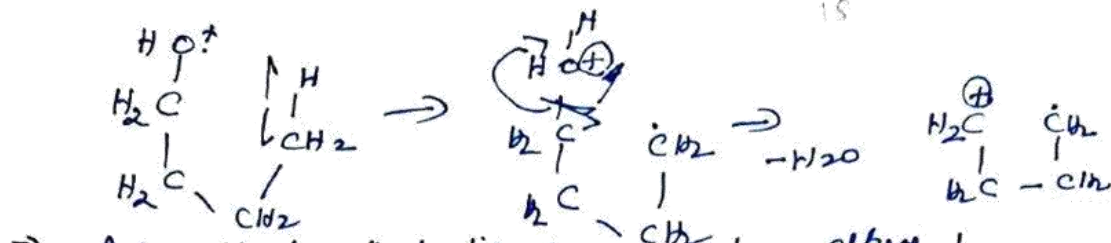
(i) The molecular ion peak of primary and secondary alcohols is usually of low abundance. It is not detected in tertiary alcohols.

(ii) The parent ion peak is formed by the removal of one electron from the lone pairs on the oxygen atom of primary and secondary alcohols.

(iii) The number of fragmentation modes in alcohols depend upon the fact whether it is primary, secondary or tertiary alcohol.

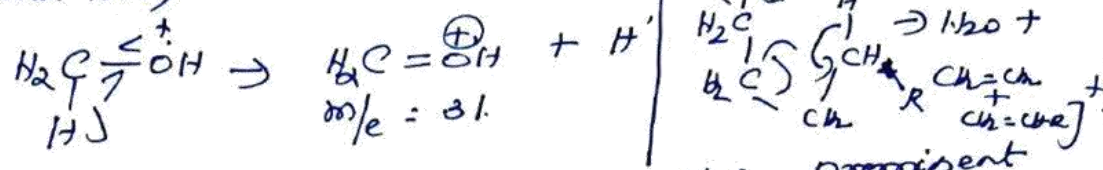
(iv)  $\alpha$ -cleavage (fragmentation of carbon-carbon bond adjacent to oxygen atom) is the preferred fragmentation mode.

(v) Primary alcohols eliminate  $\text{H}_2\text{O}$  and a peak at  $(m-18)$  due to loss of water generally occurs provided a hydrogen atom is present on  $\gamma$  or  $\beta$ -carbon atom. Thus a hydrogen atom is abstracted through a six-membered transition state from a carbon atom, four atoms away from that bearing the hydroxyl group. This is proved by deuterium labelling studies (1,4-elimination).

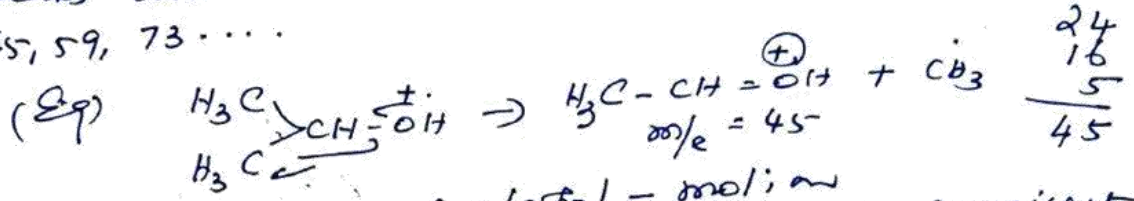


→ A concurrent elimination of water and an alkene is usually observed with alcohols containing four or longer carbon chains. →

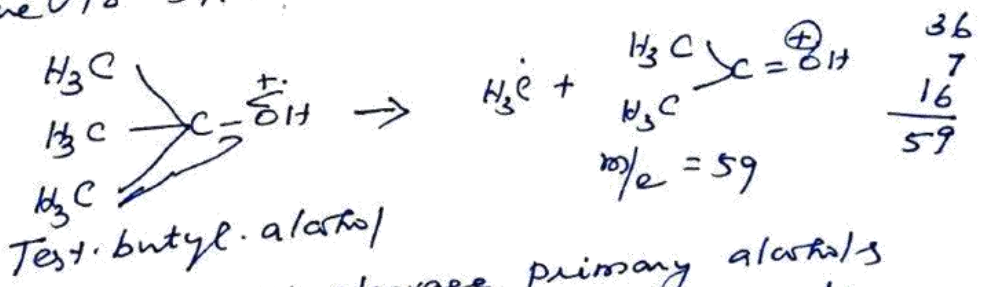
(vi) Primary alcohols show a prominent peak at  $m/e = 31$  (formation of oxonium ion)



Secondary alcohols cleave to give prominent peaks due to  $\text{R}-\text{CH}=\text{OH}^+$  at  $m/e$  values at 45, 59, 73, ...

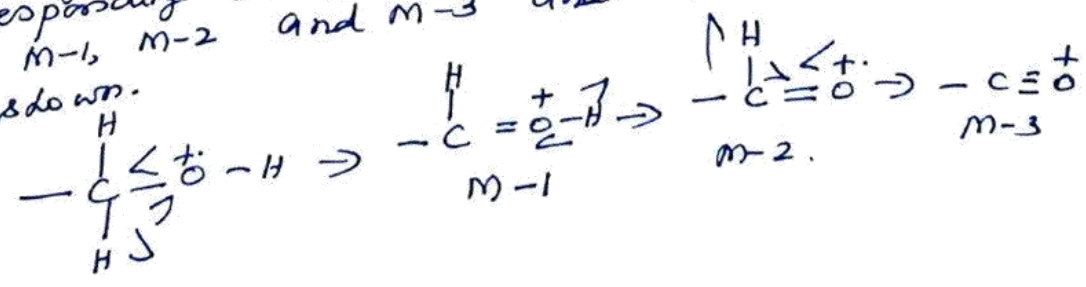


Isopropyl alcohol - molim  
Tertiary alcohols (sec) fragment to give prominent peaks due to 59, 73, 87, etc.,



(vii) In addition to  $\alpha$ -cleavage, primary alcohols also undergo  $\beta$ ,  $\gamma$ ,  $\delta$ -cleavage to form peaks at  $m/e$  values 45, 59, 73, ...

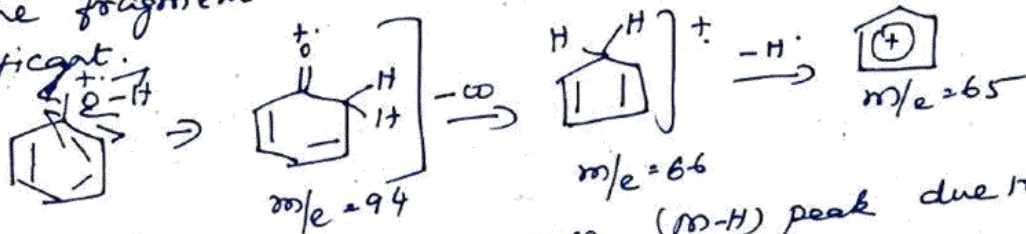
(viii) Long-chain members may show peaks corresponding to successive loss of H-radicals at  $m-1$ ,  $m-2$  and  $m-3$  and can be represented as shown.



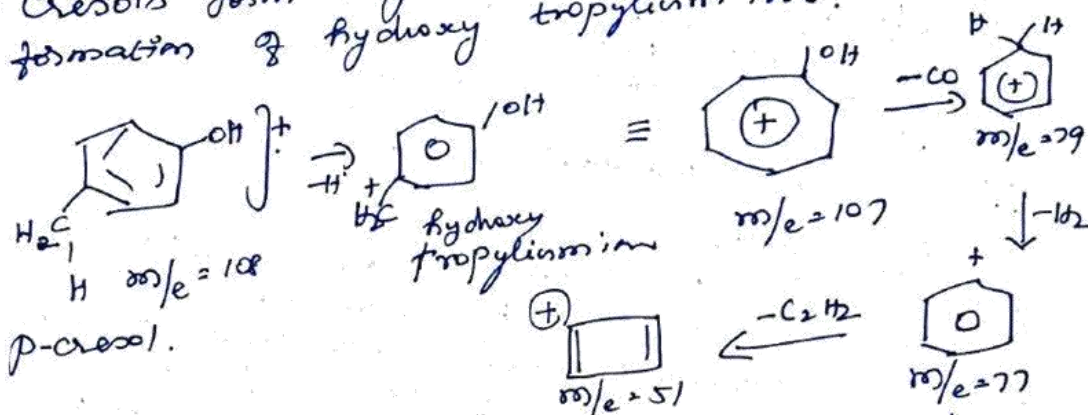
16) Explain the mass spectra of phenols.

(i) The phenols generally exhibit strong molecular ion peaks which may be the base peak.

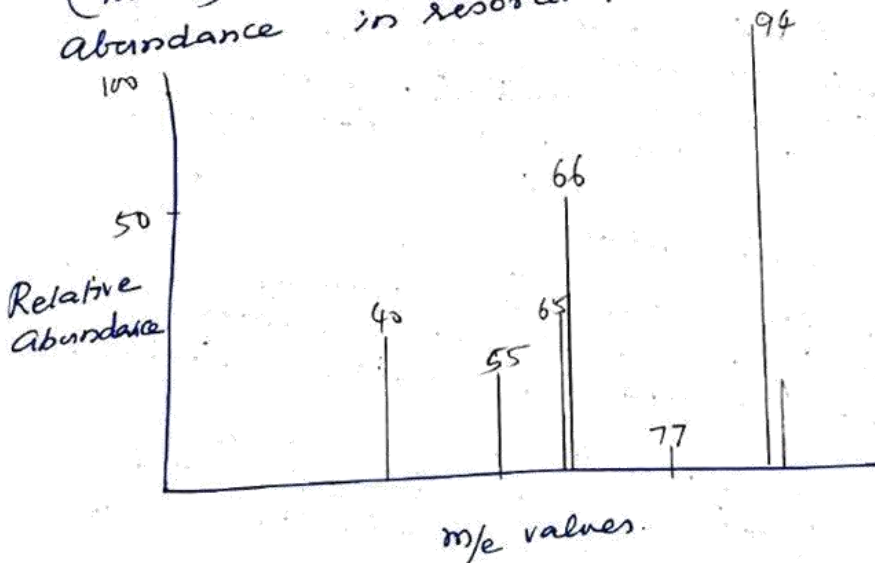
(ii) The fragment ion due to loss of CO is most significant.



(iii) Cresols form very intense (M-H) peak due to the formation of hydroxy tropylium ion.



(iv) In catechol (M-18)<sup>+</sup> peak is intense, while (M-28)<sup>+</sup> and (M-29)<sup>+</sup> peaks are formed in abundance in resorcinol and quinol.



17. Explain the mass spectrum of hydrocarbons and carbonyl compounds (aldehydes & ketones).

(a) Alkanes:- (Saturated hydrocarbons)

(i) Straight chain alkanes show low-intensity molecular ion peaks. The peaks are most intense in the  $C_2-C_5$  range.

(ii) Groups of peaks in the mass spectrum are observed 14 mass units apart. The intensities of these peaks decrease with increasing molecular weight.

(iii) Straight chain alkanes rarely eliminate methyl groups and consequently peaks corresponding to  $(m-15)$  are not observed.

(i) The most abundant peaks correspond to

$C_nH_{2n+1}$  ion.

(iv) There is no preferred charge stabilisation site to favour any specific cleavage.

(v) Less abundant peaks correspond to  $C_nH_{2n}$  and  $C_nH_{2n-1}$  ions are also observed.

(vii) The relative abundance of fragment ions formed depends upon

(i) stability of the ion formed and  
(ii) the stability of the radical which is lost.

(viii) Greater the dispersal of odd electron, greater is the stability of free radical. n-butyl free radical is more stable than n-propyl free radical.

(b) Branched chain alkanes:-

(i) Bond cleavage takes place preferably at the site of branching. Due to such cleavage, a more stable secondary or tertiary carbanion is formed.

(ii) Largest substituent at a branch is eliminated readily as a radical. The radical achieves stability by the delocalisation of lone electron.

(iii) The relative abundance of parent ion is least and mostly not observed.

(iv) Great number of fragments result from a

branched chain compound compared to the straight chain compound. It is due to greater pathways available for cleavage.

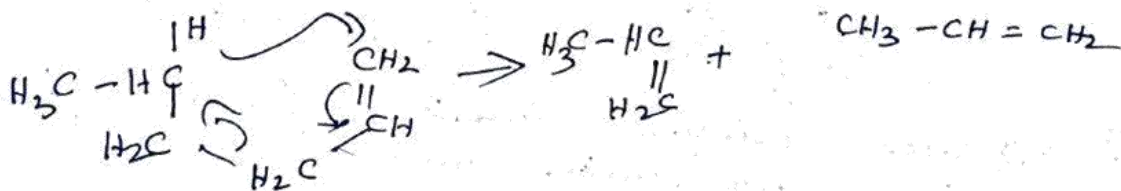
### (c) Dienes (Unsaturated hydrocarbons)

(i) The molecular ion peak in the spectra of unsaturated compounds is more intense than the corresponding saturated compounds. The reason is the better resonance stabilisation of the charge on the cation formed by the removal of one of  $\pi$  electrons.

(ii) The molecular ion peak is less intense and the most intense peak is due to stable charged species produced by allylic cleavage (cleavage at the  $\beta$ -bond) with the positive charge usually remaining with the fragment containing the double bond.

(iii) If the formation of six-membered cyclic transition state is possible, Mc-Lafferty rearrangement usually occurs.

(e.g.) 1-hexene undergoes Mc-Lafferty rearrangement.



### (d) Alkynes:-

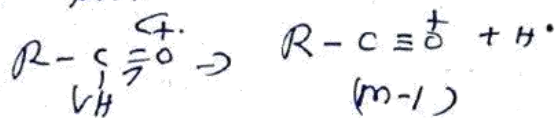
For 1-butyne and 2-butyne, the molecular ion peak is the base peak. The relative abundance of the molecular ion peak decreases as the molecular mass of the alkyne increases. The fragment ions are formed generally by the loss of alkyl radicals. Thus  $M-15$ ,  $M-29$  etc. peaks are generally formed.

## Aldehydes & ketones:-

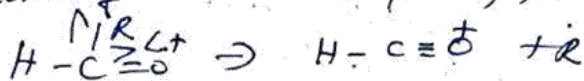
### (a) Aliphatic aldehydes & ketones:-

- (i) The intensity of the molecular ion peak decreases as the alkyl chain length increases.
- (ii) The major fragmentation processes are  $\alpha$  and  $\beta$ -cleavage. In  $\alpha$ -cleavage, the bigger group on either side of the carbonyl group is preferably lost.  $\alpha$ -cleavage leads to

~~(i)~~ acylium ion.



Loss of R also occurs resulting in the formation of  $H-\overset{\overset{+}{C}}{\equiv O}$  (m/e = 29)



Thus the peaks (m-1) and at m/e = 29 are characteristic of aldehydes. The peak at m/e = 29 from higher aldehyde may also be due to  $C_2H_5^+$

~~(ii)~~ Heterolytic  $\beta$ -cleavage leads to a peak at m/e = 43

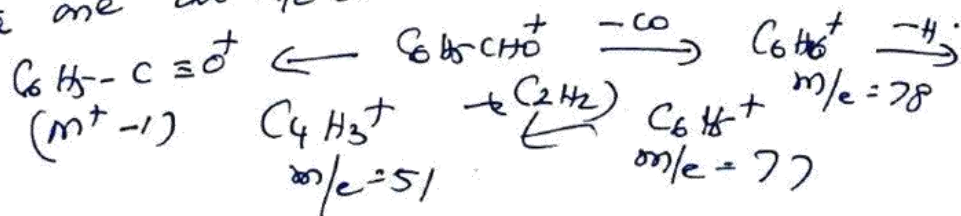


(iii) Aliphatic aldehydes bearing a  $\gamma$ -hydrogen, the characteristic fragmentation mode is Mc-Lafferty rearrangement

### (b) Aromatic aldehydes:-

- (i) Aromatic aldehydes exhibit a very intense molecular ion peak.
- (ii) The loss of hydrogen via  $\alpha$ -cleavage is a very favorable process. For (29) in the mass spectrum of benzaldehyde, (m-1) peak due to m/e = 105 is the base peak.

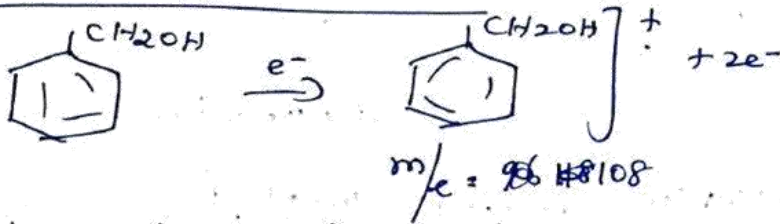
(iii) Peak at m/e 77 due to  $C_6H_5^+$  followed by the one at m/e 51 due to  $C_4H_3^+$ .





18) Explain the mass fragmentation of benzyl alcohol.

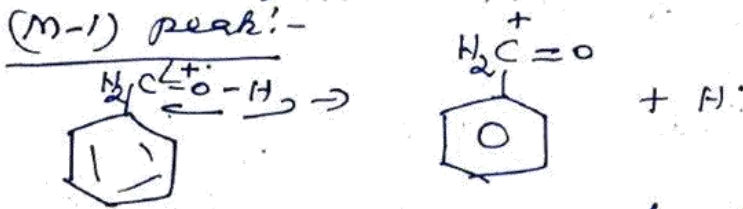
1) Molecular ion peak:-



72  
8  
16  
96  
12  
118

Various fragments are:-

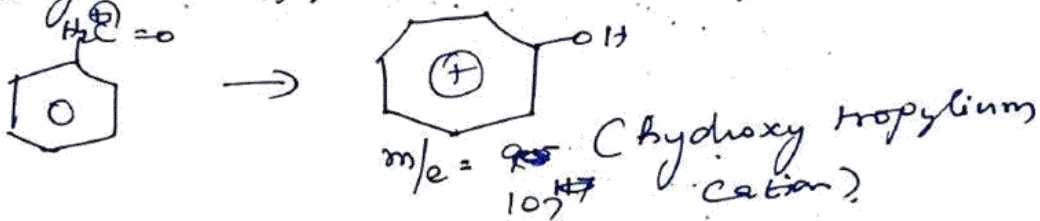
2) (M-1) peak:-



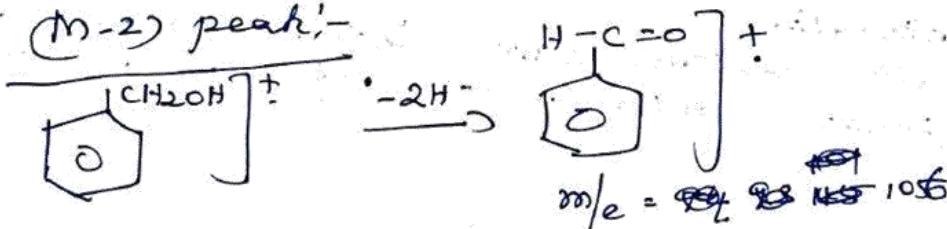
84  
8  
1.6  
8  
108

(M-1) peak  $m/e = 107$

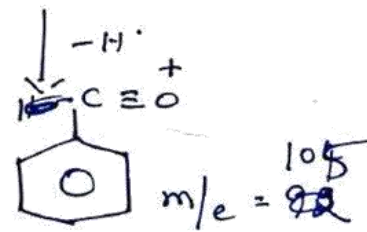
The formed (M-1) peak rearranges to form hydroxy tropylium ion.



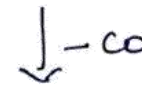
3) (M-2) peak:-



84  
1.6  
101



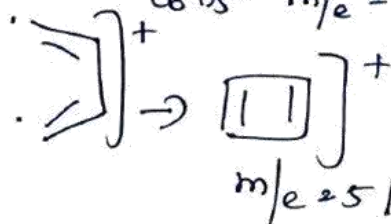
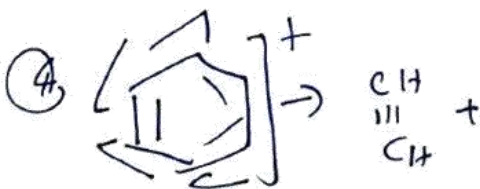
115  
28  
87  
84  
16  
100



12  
16  
28



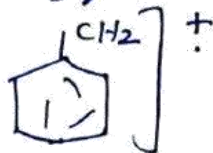
104  
28  
76



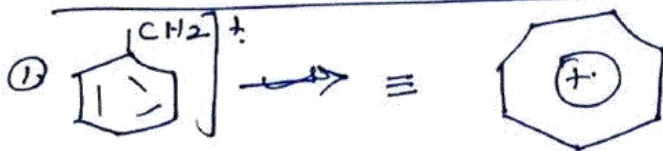
100  
28  
72



25  
 (19) Explain the mass fragmentation of benzyl radical ion.



(1) ~~molecular ion peak~~:-



Tropylium radical ion

$m/e = 91$ .

more Benzyl radical ion rearranges to a more stable tropylium radical ion which appears at  $m/e$  value of 91.

stable since it is stabilised by resonance

(2) It loses acetylene and forms  $C_5H_5^+$  at  $m/e = 65$

