

PROSPERITY ACADEMY

AS CHEMISTRY 9701

Crash Course

RUHAB IQBAL

**ANALYTICAL
CHEMISTRY**

COMPLETE NOTES



0331 - 2863334



**ruhab.prosperityacademics
@gmail.com**



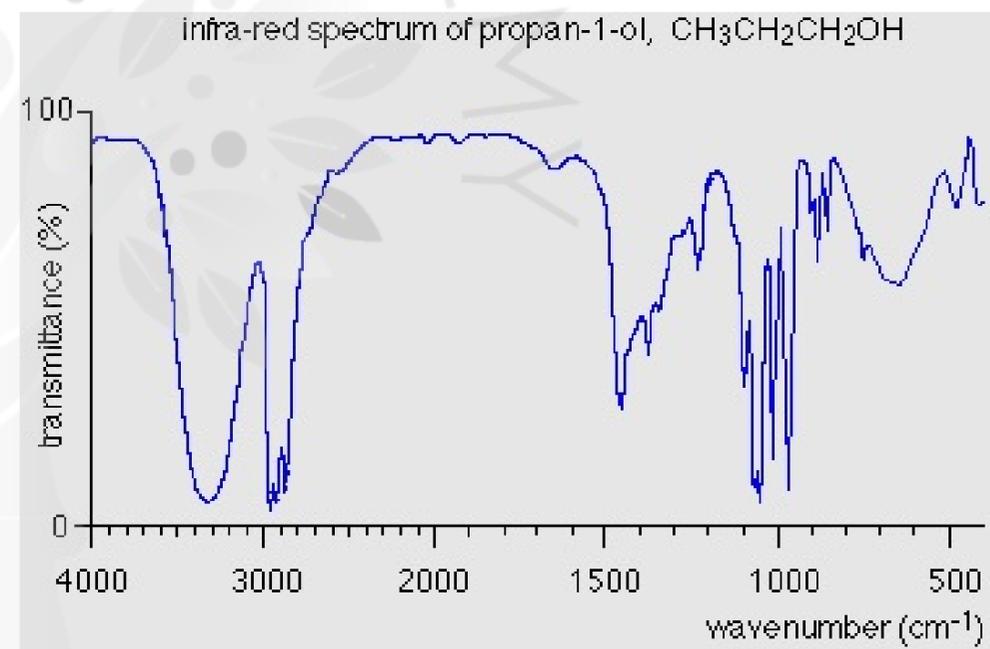
Infrared Spectroscopy:-

- Different bonds absorb different infrared frequencies
- Therefore shining frequencies of IR on a sample and placing a sensor behind will show us how much of each frequency has been transmitted (Known as % transmittance)
- The plot can be used to work out the bonds in an unknown sample

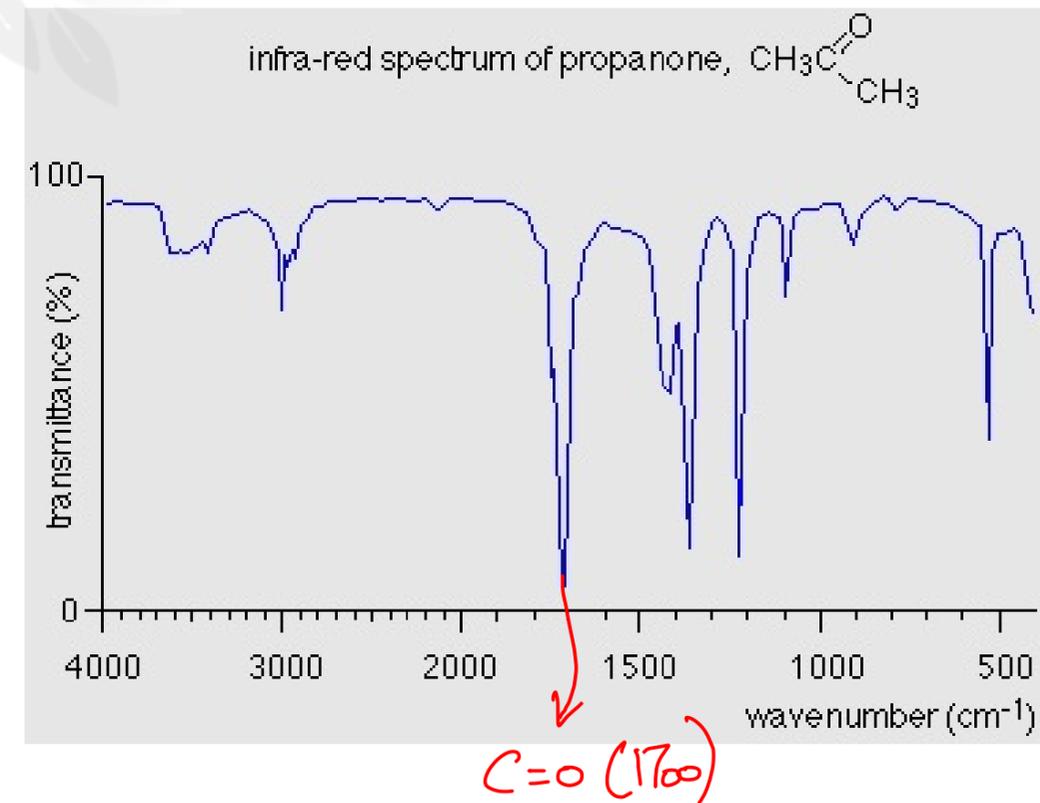
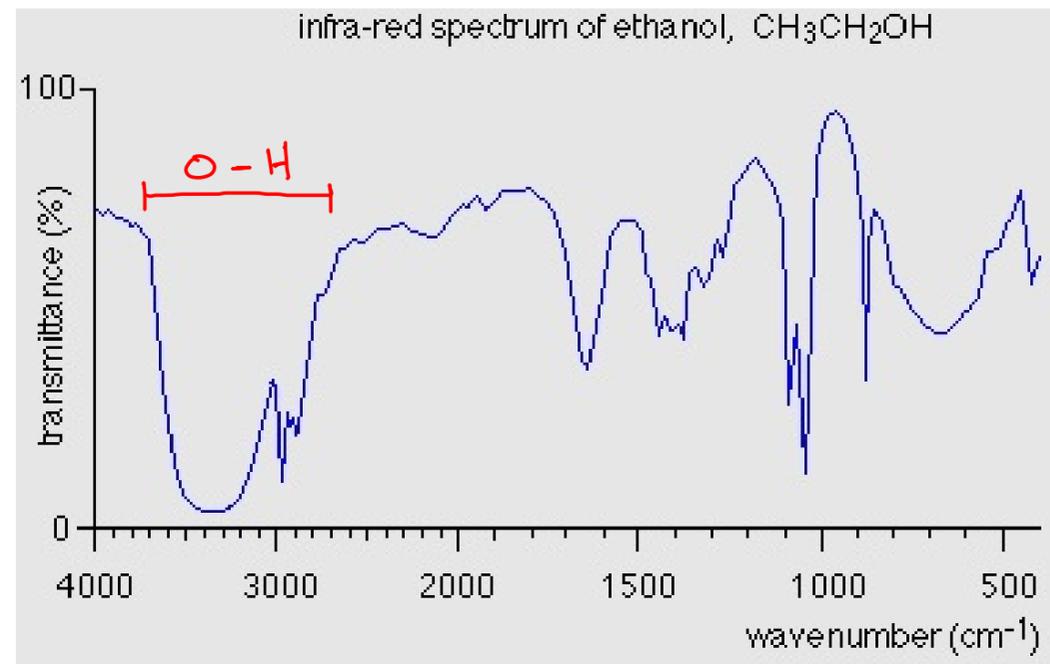
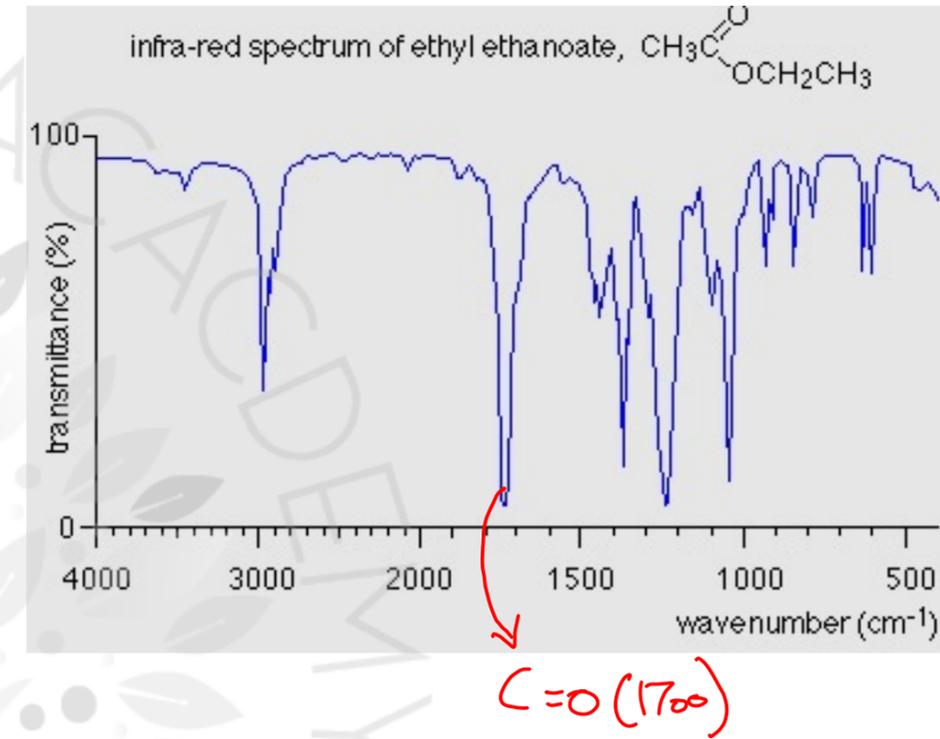
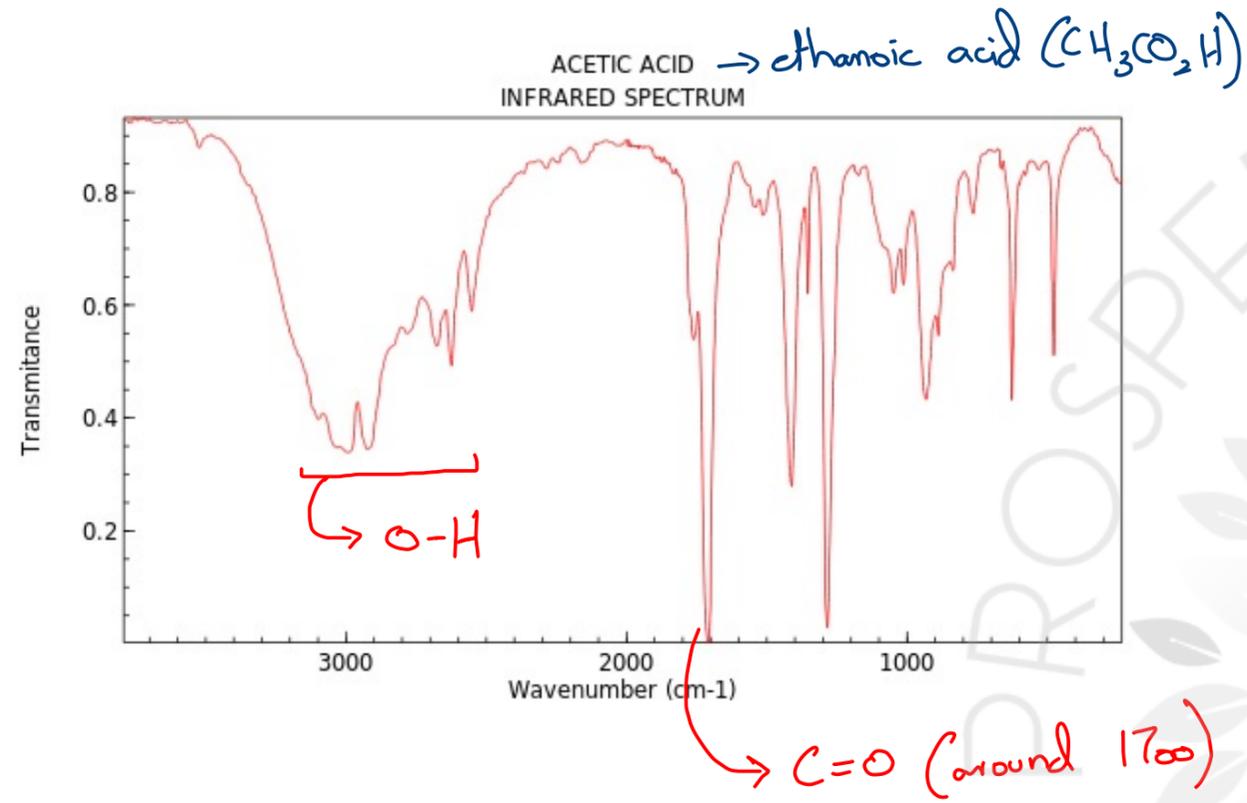
8 Characteristic infra-red absorption frequencies for some selected bonds

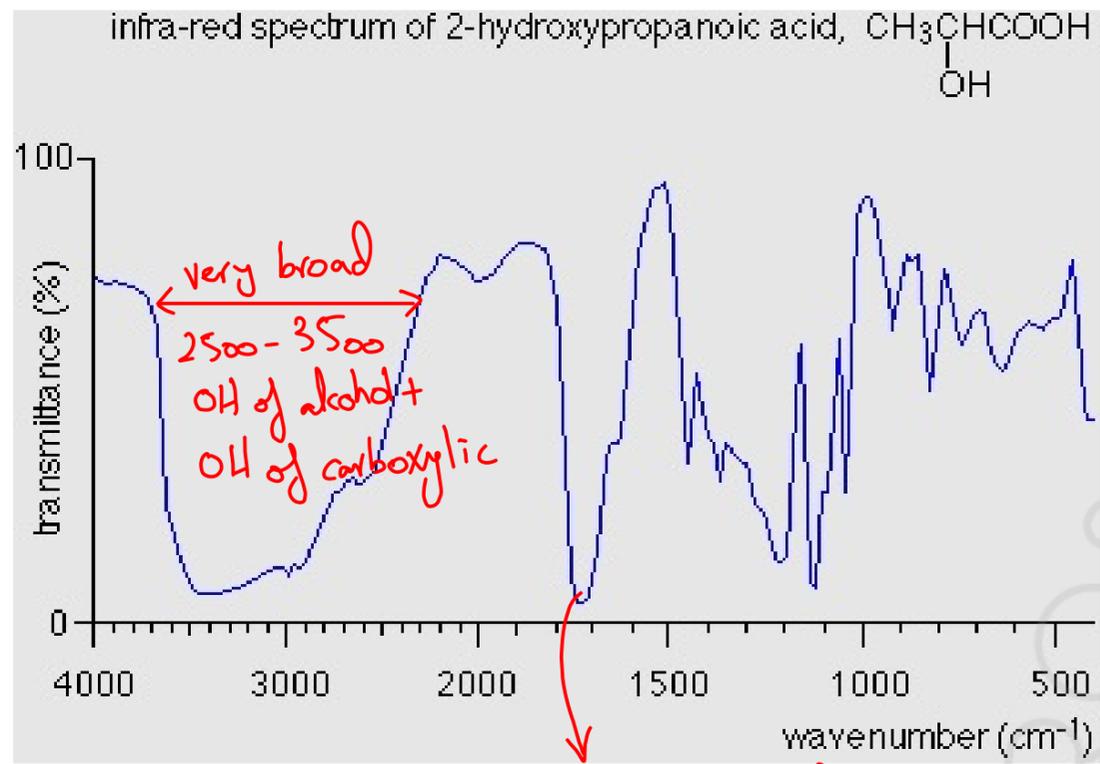
→ will be given where needed

Bond	Functional groups containing the bond	Absorption range (in wavenumbers)/cm ⁻¹	Appearance of peak (s = strong, w = weak)
C-O	alcohols, ethers, esters	1040-1300	s
*C=C	aromatic compounds, alkenes	1500-1680	w unless conjugated
*C=O	amides ketones and aldehydes esters	1640-1690 1670-1740 1710-1750	s s s
C≡C	alkynes	2150-2250	w unless conjugated
C≡N	nitriles	2200-2250	w
C-H	alkanes, CH ₂ -H alkenes/arenes, =C-H	2850-2950 3000-3100	s w
*N-H	amines, amides	3300-3500	w
*O-H	carboxylic acids, RCO ₂ -H H-bonded alcohol, RO-H free alcohol, RO-H	2500-3000 3200-3600 3580-3650	s and very broad s s and sharp



Easily distinguishable groups and important frequencies to always look out for:-



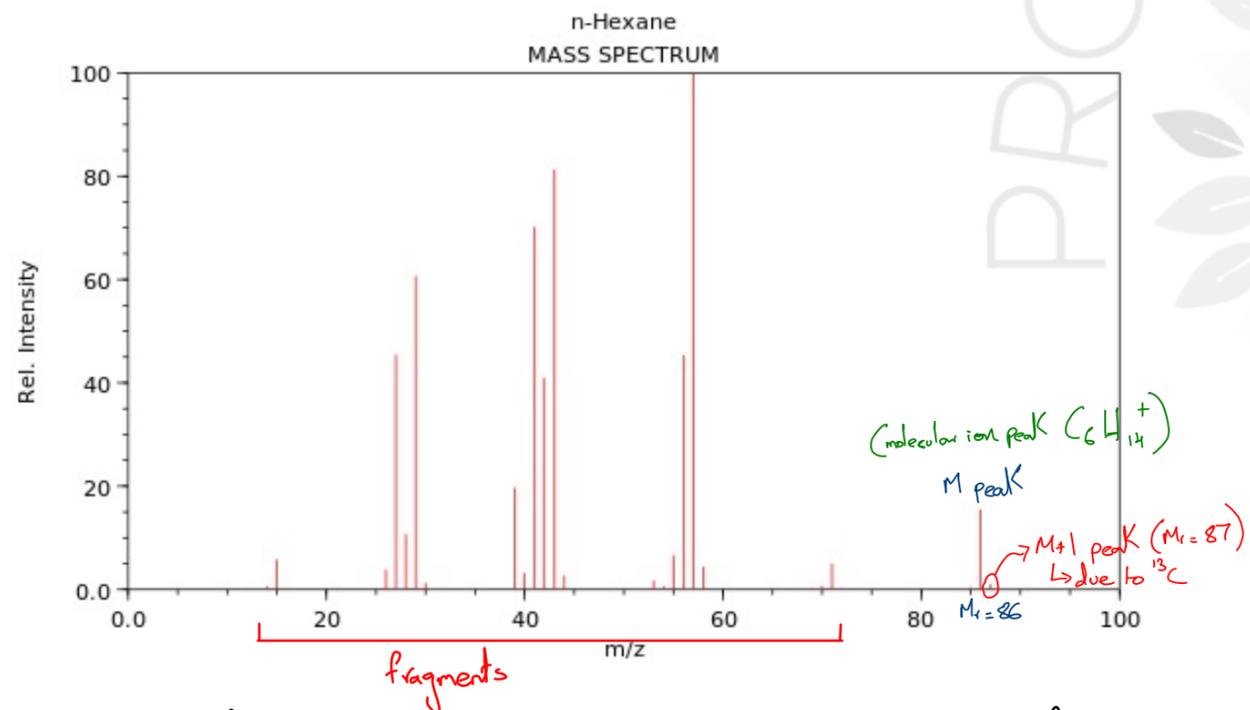


- 1) Focus at 1700 (C=O)
- 2) Focus in 2500 - 3500 range (O-H)
Carboxylic: 2500-3000 Alcohol: 3200-3600

Mass Spectrometry:- We can perform mass spectrometry on an organic sample and get to know of:-

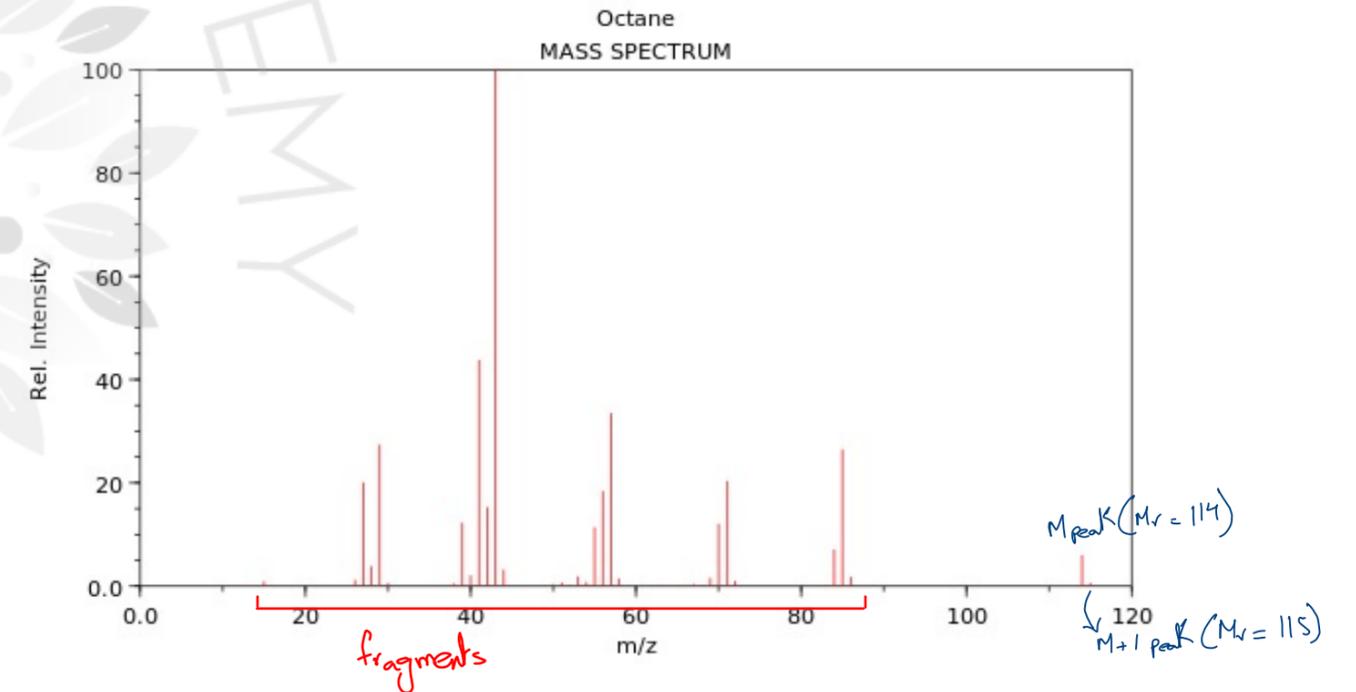
- 1) Its M_r
- 2) The no. of C atoms in it
- 3) Whether or not the compound has Cl or Br
- 4) Fragments

1) Working out M_r and number of C atoms:-



Q. The abundance of the M peak is 22%. The abundance of the M+1 peak is 1.45. How many C atoms are present in the sample?

$$\begin{array}{l}
 M : M+1 \\
 100 : 1.1n \\
 22 : 1.45 \\
 n = 5.99 \approx 6 \text{ C atoms}
 \end{array}$$



Q. The abundance of the M peak is 23%. The abundance of the M+1 peak is 2%. How many C atoms are present in the sample?

$$\begin{array}{l}
 M : M+1 \\
 100 : 1.1n \\
 23 : 2 \\
 n = 7.9 \approx 8 \text{ C atoms}
 \end{array}$$

2) Cl or Br?

- If a compound has Cl or Br, it will also give an $M+2$ peak as Cl has isotopes ^{35}Cl and ^{37}Cl and Br has isotopes ^{79}Br and ^{81}Br

- If Cl is present:-
 $M : M+2$
 $3 : 1$

- If Br is present:-
 $M : M+2$
 $1 : 1$

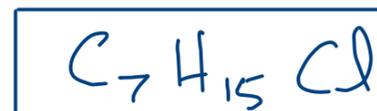
Q. The mass spectrum of an organic compound has a molecular ion peak at 134 with an abundance of 20%. It also shows a peak at 135 and 136 with abundances 1.54% and 6.67% respectively. Given the molecular formula of the compound is $\text{C}_x\text{H}_y\text{X}$ where X is a halogen, deduce its exact molecular formula.

$$\begin{array}{l} M : M+1 \\ 100 : 1.1n \\ 20 : 1.54 \\ n = 7 \text{ C atoms} \end{array}$$

$$\begin{array}{l} M : M+2 \\ 20 : 6.67 \\ 3 : 1 \\ \text{therefore Cl} \end{array}$$

$$\begin{array}{r} 134 \\ \text{Br} :- \underline{-35} \\ 99 \end{array}$$

$$99 - 7(12) = 15 \text{ H atoms}$$



3) Fragmentation :-

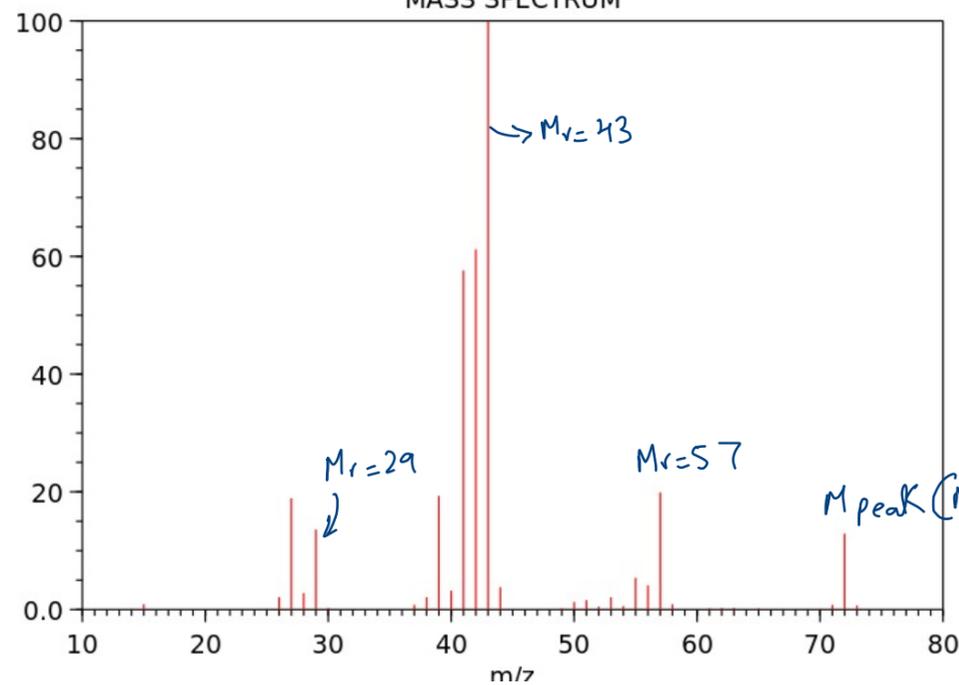
- The molecular ion is unstable and can break into smaller pieces :-
- Upon fragmentation the compound breaks into a positive ion and free radical
- Many combinations of fragmentation are possible



↑ produces line

↪ does not produce line

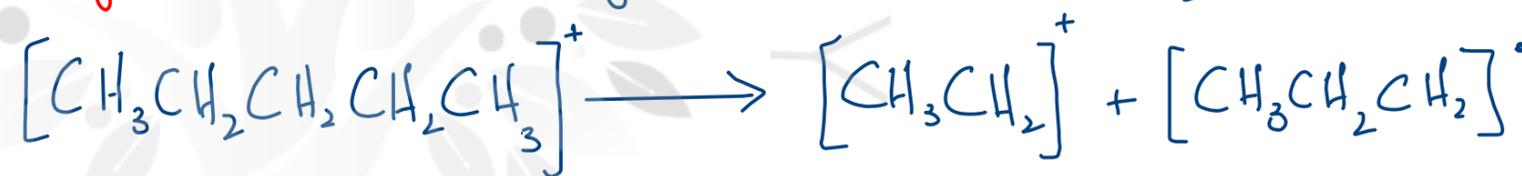
Pentane (CH₃CH₂CH₂CH₂CH₃ Mr=72)
MASS SPECTRUM



Q. Identify the fragments for peaks at 29, 43 and 57 and construct equations to show how they were formed.

- $12 \times 2 = 24$
 \downarrow Mr of C \downarrow atoms
 C atoms

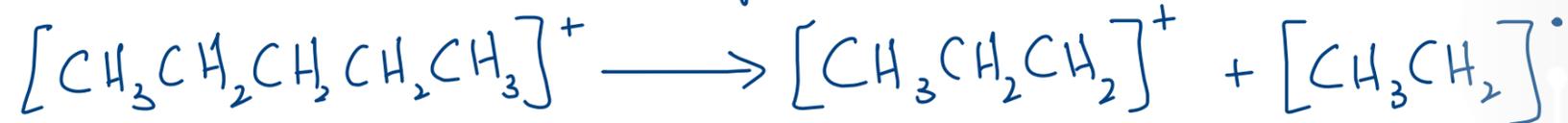
- $29 - 24 = 5 \rightarrow$ H atoms
 fragment at 29 \rightarrow [CH₃CH₂]⁺



- $12 \times 3 = 36$

$43 - 36 = 7$

fragment at 43 = [CH₃CH₂CH₂]⁺



- Examiner will provide enough information and only ask stuff that's doable, don't worry!

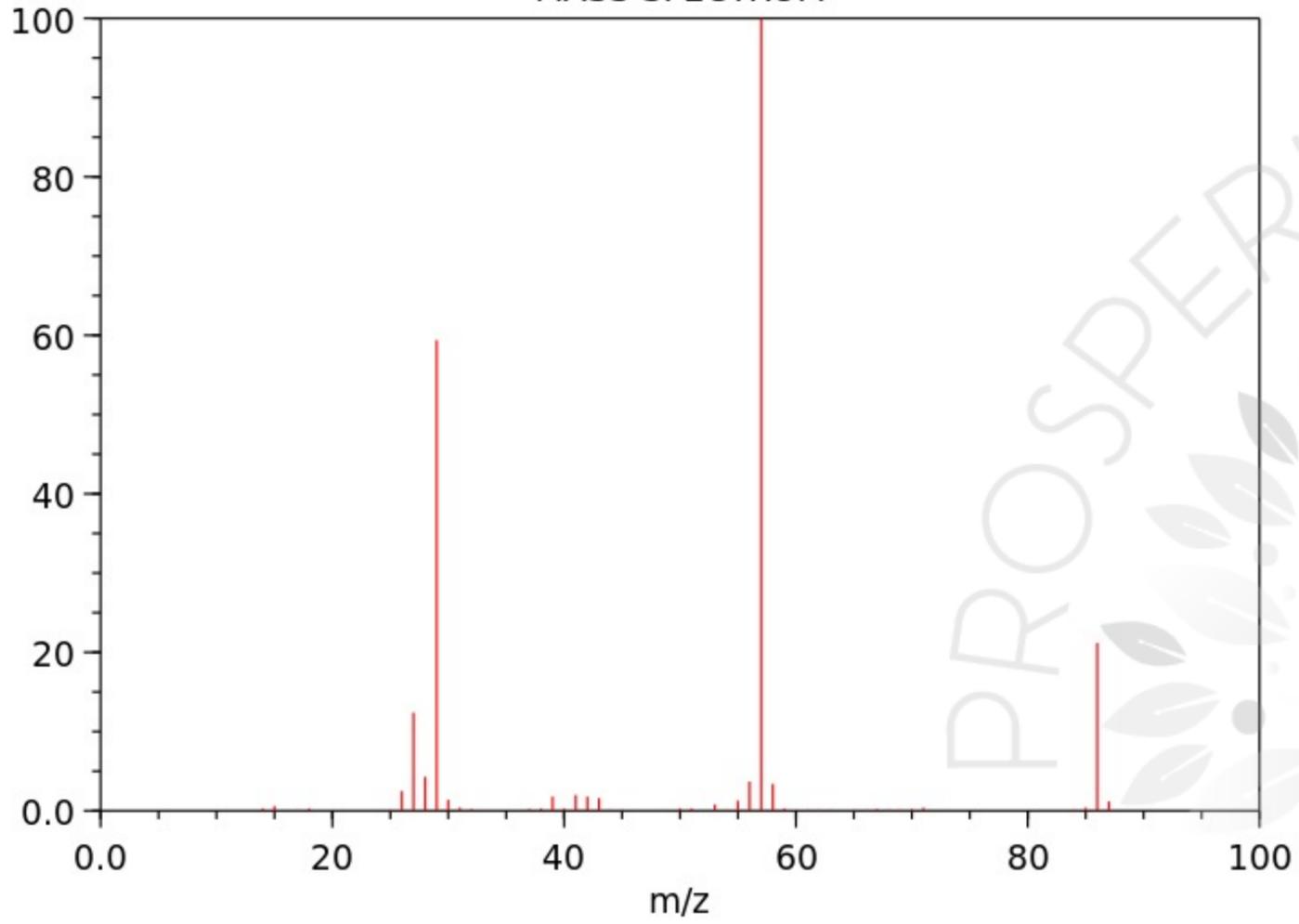
- $12 \times 4 = 48$

$57 - 48 = 9$

fragment at 57 = [CH₃CH₂CH₂CH₂]⁺



3-Pentanone
MASS SPECTRUM



Q. Identify the fragments at 57 and 29 and construct equations.



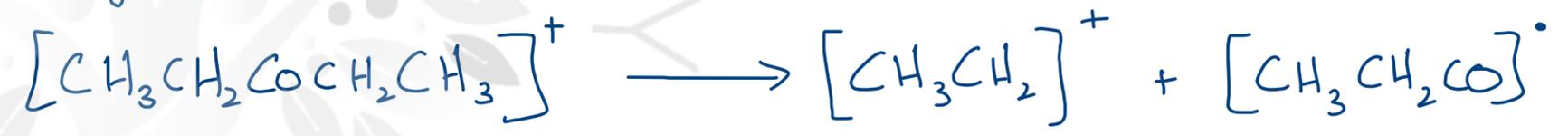
$(12 \times 2) + 5 = 29$

$(12 \times 3) + 5 + 16 = 57$

- fragment at 57 = $[\text{CH}_3\text{CH}_2\text{C}=\text{O}]^+$



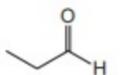
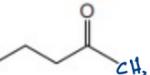
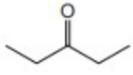
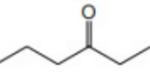
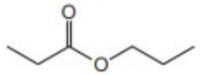
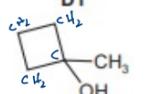
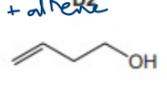
- fragment at 29 = $[\text{CH}_3\text{CH}_2]^+$



3 Organic compounds can be distinguished using chemical tests and analytical techniques.

(a) Table 3.1 shows four pairs of organic compounds.

Table 3.1

organic compounds		reagent	positive result of chemical test on identified compound
aldehyde A1 	ketone A2 	Tollen's reagent	silver mirror with A1
methyl ketone B1 	ketone B2 	$I_2(aq) + NaOH(aq)$	yellow precipitate with B1
ketone C1 	ester C2 	2,4-DNPH	yellow precipitate with C1
tertiary alcohol D1 	primary alcohol + alkene D2 	Aqueous Br_2	- Solution turns from brown to colourless with D2

- (i) Complete Table 3.1 to:
- identify a reagent which can distinguish between the compounds in each pair
 - give the **positive** result of the chemical test **and** identify which compound shows this result.

Use a different reagent for each test.

[8]

- (ii) A1 and A2 are structural isomers.

Define structural isomers.

Compounds having the same molecular formula but different structural formula.

[1]

- (iii) Give the systematic name of B2.

pentan-3-one

[1]

- (iv) Deduce the molecular formula of D1.

$C_5H_{10}O$

[1]

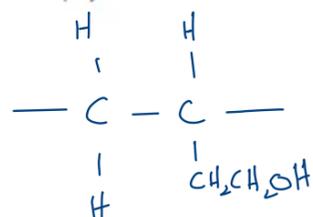
(b) D2 forms polymer Z when heated gently.

- (i) Identify the type of polymer that forms from D2.

addition polymer

[1]

- (ii) Draw one repeat unit of polymer Z.



[2]

(c) Organic compound E contains three carbon atoms.

E reacts with cold dilute acidified $KMnO_4(aq)$ to form a single compound F with $M_r = 154.9$.

Fig. 3.1 shows the infrared spectrum of E.

Fig. 3.2 shows the infrared spectrum of F.

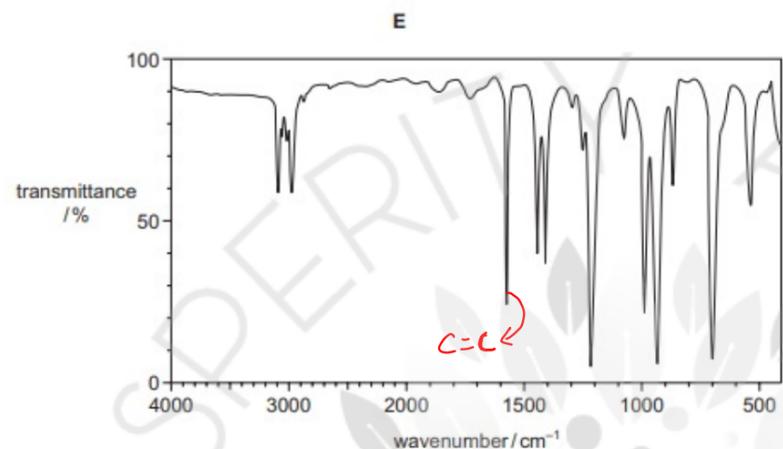


Fig. 3.1

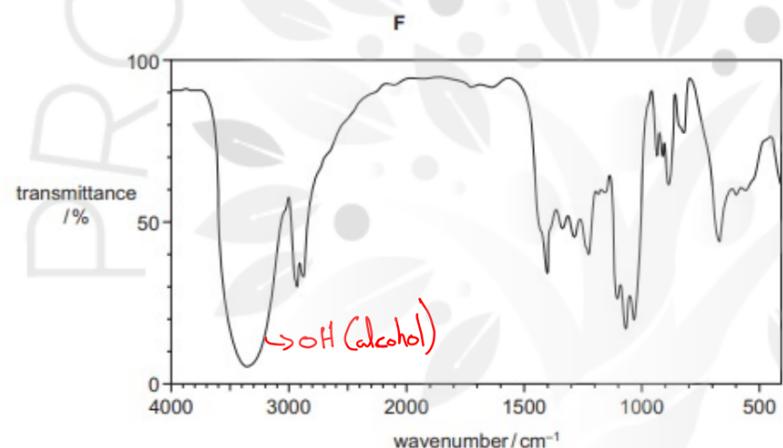


Table 3.2

bond	functional group containing the bond	characteristic infrared absorption range (in wavenumbers)/ cm^{-1}
C-O	hydroxy, ester	1040-1300
C=C	aromatic compound, alkene	1500-1680
C=O	amide, carbonyl, carboxyl, ester	1640-1690 1670-1740 1710-1750
C≡N	nitrile	2200-2250
C-H	alkane	2850-3100
N-H	amine, amide	3300-3500
O-H	carboxyl, hydroxy	2500-3000 3200-3650

Both spectra show absorptions between 2850 and 2950 cm^{-1} owing to C-H bonds in each molecule.

- (i) Use the two infrared spectra and Table 3.2 to identify the functional group present only in E.

Explain your answer, referring only to absorptions at frequencies greater than 1500 cm^{-1} .

functional group $C=C$

explanation absorption in between 1500-1600

[1]

- (ii) Use the infrared spectrum of F to identify the functional group formed when E reacts with cold dilute acidified $KMnO_4(aq)$.

Explain your answer, referring only to absorptions at frequencies greater than 1500 cm^{-1} .

functional group Alcohol

explanation absorption at 3200-3650

[1]

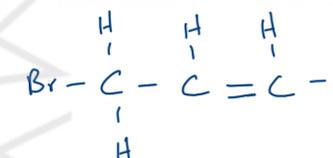
- (iii) The mass spectrum of E shows a molecular ion peak and an M+2 peak of approximately equal abundance at $m/e = 120$ and 122.

Deduce the relative molecular mass, M_r , of E.

$M_r = 120$

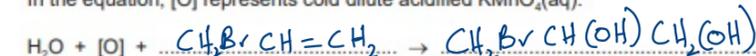
[1]

- (iv) Use the information in 3(c) to suggest a structure for E.



[1]

- (v) Complete the equation for the reaction of E with cold dilute acidified $KMnO_4(aq)$ to form F. In the equation, [O] represents cold dilute acidified $KMnO_4(aq)$.



[1]

- (d) C2 can be synthesised using A1 as a single organic reactant.



Devise a multi-step synthetic route to form C2 from A1.

Identify relevant reagents and conditions, and state the organic products of each step.

Step 1:- Separate a sample of A1 and reduce it using $LiAlH_4$ in dry ether. The product will be $CH_3CH_2CH_2OH$.

Step 2:- Separate a sample of A1 and oxidise it under heat under reflux with $K_2Cr_2O_7$ and then distill the product CH_3CH_2COOH .

Step 3:- React $CH_3CH_2CH_2OH$ and CH_3CH_2COOH in a test tube with gentle heating and few drops of conc. H_2SO_4 to get C2.

[Total: 22]

- 5 Lactones are cyclic esters. Under suitable conditions, lactones form from molecules that have both an alcohol and a carboxylic acid functional group. Equation 1 shows an example of the formation of a lactone.

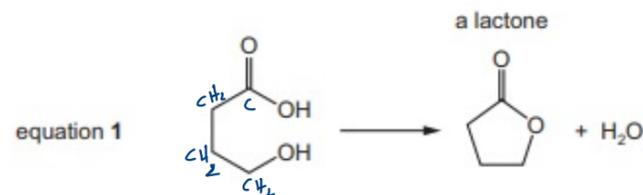


Fig. 5.1 shows the synthesis of lactone P from compound M.

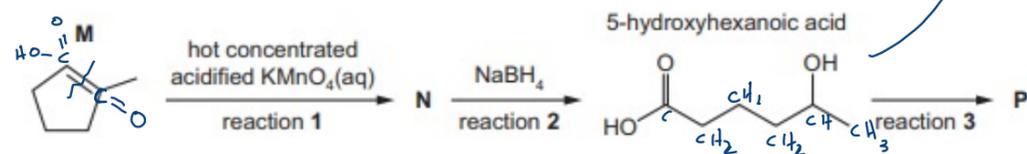
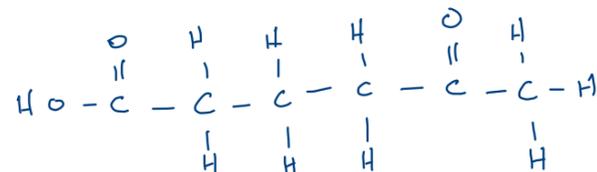


Fig. 5.1

- (a) (i) M reacts with hot concentrated acidified $\text{KMnO}_4(\text{aq})$ to form N, $\text{C}_6\text{H}_{10}\text{O}_3$, in reaction 1.

Draw the structure of N.



[1]

- (ii) N is reduced by NaBH_4 to form 5-hydroxyhexanoic acid in reaction 2.

Construct an equation for reaction 2 using molecular formulae.

In the equation, use [H] to represent one atom of hydrogen from the reducing agent.



[1]

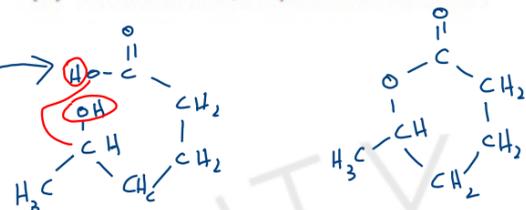
- (iii) Reaction 2 is a nucleophilic addition.

Suggest why reaction 2 creates a mixture of two organic compounds.

N is planar so can be attacked from either side which gives rise to 2 optical isomers

[2]

- (iv) Draw lactone P, the product of reaction 3.



[1]

- (b) A student monitors the progress of reaction 2 using infrared spectroscopy.

Use Table 5.1 to suggest why it is difficult to distinguish between N and 5-hydroxyhexanoic acid using infrared spectroscopy.

Except for the $\text{C}=\text{O}$ and OH (alcohol) bonds, all other bonds are similar and the absorptions will overlap making it indistinguishable

[2]

Table 5.1

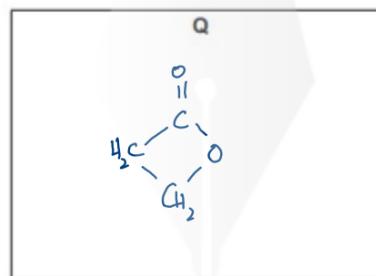
bond	functional group containing the bond	characteristic infrared absorption range (in wavenumbers)/ cm^{-1}
C-O	hydroxy, ester	1040-1300
C=C	aromatic compound, alkene	1500-1680
C=O	amide carbonyl, carboxyl ester	1640-1690 1670-1740 1710-1750
C≡N	nitrile	2200-2250
C-H	alkane	2850-3100
N-H	amine, amide	3300-3500
O-H	carboxyl hydroxy	2500-3000 3200-3650

- (c) Unknown lactone Q is analysed using mass spectrometry. Table 5.2 shows information from the mass spectrum.

Table 5.2

peak	m/e	abundance
M+	72	95.5
M+1	73	3.15

Use these data to deduce the structure of Q. Show your working.



$$\frac{100}{95.5} : \frac{1.1n}{3.15} \quad n = 2.99 \approx 3$$

[2]

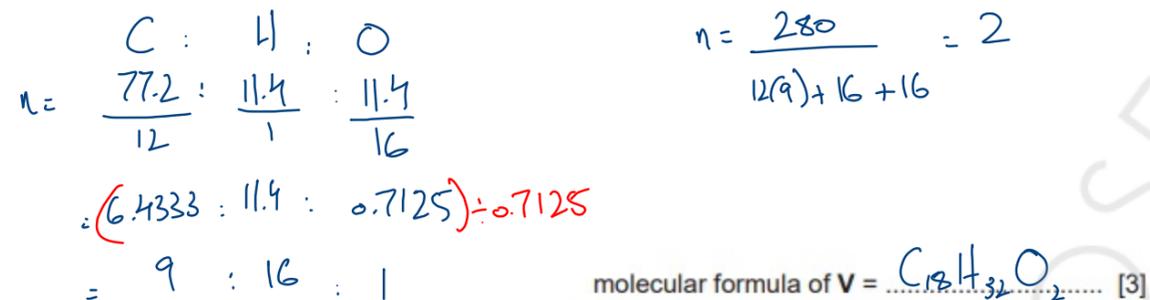
[Total: 9]

4 Compound V is a liquid.

V contains 77.2% carbon, 11.4% hydrogen and 11.4% oxygen by mass.

V has a relative molecular mass of 280.

(a) Calculate the molecular formula of V. Show your working.



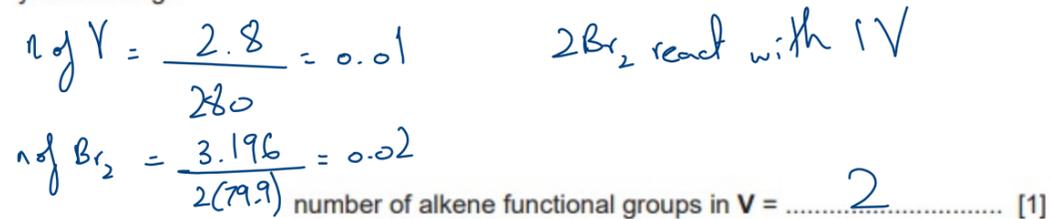
(b) V contains two types of functional group: a carboxylic acid and an alkene.

(i) Describe a chemical test and observation which confirms the presence of a carboxyl functional group.

Add $Na_2CO_3(aq)$, effervescence of CO_2 gas will be observed [2]

(ii) A 3.196 g sample of Br_2 reacts completely with 2.800 g of V.

Calculate how many alkene functional groups are present in one molecule of V. Show your working.



(c) W, X and Y have the same molecular formula, $C_5H_{10}O$.

W, X and Y are added separately to different reagents. Observations for these reactions are described in Table 4.1.

	+ 2,4-dinitrophenylhydrazine	+ alkaline $I_2(aq)$	+ Fehling's reagent and warm
W	orange precipitate seen	no change	orange-red precipitate seen
X	orange precipitate seen	yellow precipitate seen	no change
Y	orange precipitate seen		

(i) W, X and Y each contain a common functional group.

Name the functional group that is present in all three compounds.

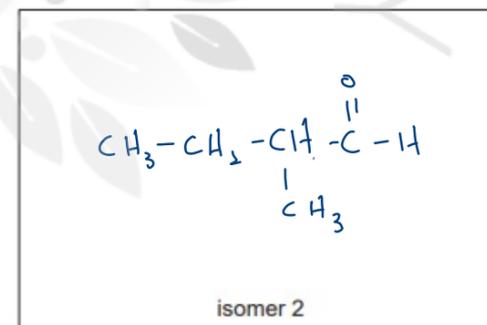
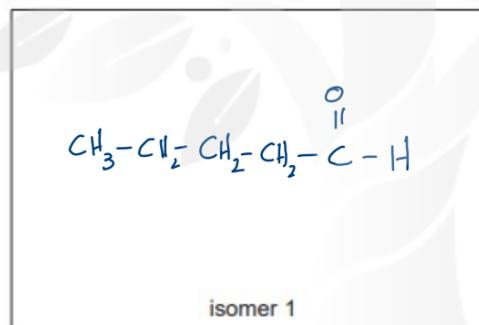
carbonyl [1]

(ii) State the formula of the yellow precipitate produced when X is added to alkaline $I_2(aq)$.

CHI_3 [1]

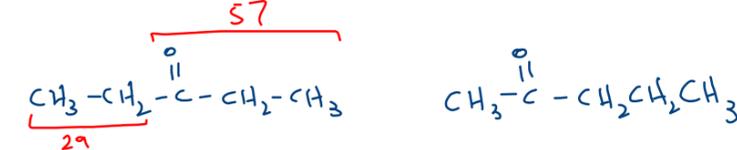
(iii) W could be one of four structural isomers.

- Draw the skeletal formulae for two possible structural isomers of W.
- Describe the type of structural isomerism shown.



type of structural isomerism

chain isomerism [3]



(d) Fig. 5.1 shows the mass spectrum of ketone Z, $C_5H_{10}O$.

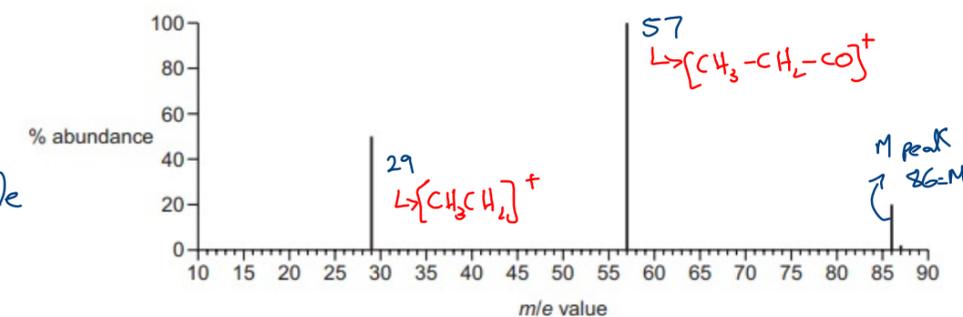


Fig. 5.1

Use the information in Fig. 5.1 to suggest the formulae of the fragments with m/e peaks at 29 and 57. Deduce the identity of Z.

$m/e = 29$ $[CH_3CH_2]^+$

$m/e = 57$ $[CH_3CH_2CH_2CO]^+$

identity of Z pentan-3-one [3]

[Total: 14]