Characteristic mass spectral fragmentation

In mass spectrometry, organic molecules that are present in the gaseous state are bombarded with a beam of energetic electrons (70eV). During bombardment pressure is maintained between 10-7 to 10-5 and electrically heated tungsten or rhenium filament is used for producing beam of electrons. Cations and many other fragments are produced due to the breakdown of the molecules. Cations further breakup to produce smaller ions. In the electric field, all these ions are accelerated and in the variable magnetic field deflection occurs depending on their ratio of mass to charge which can be sorted out and recorded. Mass spectrum is the output with mass to charge ratio on X-axis and relative abundance on Y-axis. Each line in the spectrum represents the mass of particular atom or molecule. The highest intense peak is taken as 100. It is called the base peak and the remaining peaks are expressed by comparing with the base peak.

Mass spectrometry can be used to identify the compound with the help of molecular weight, molecular formula and fragmentation pattern provided from the spectrum. It can also be used to distinguish cis and trans ions, analysis of trace elements in minerals and alloys.

PROCEDURE:

The mass spectrometer was set up according to the instructions verbally provided.

RESULTS:

The system automatically assigned m/z values to the peaks and evaluated the fragmentation pattern by arbitrarily assigning the major peak (base

peak) an intensity of 100 and expressing the other peak intensities as percentages of the base intensity.

DISCUSSION:

Identify the molecular ion peak and isotope peaks, if possible. Identify the species giving rise to peaks with relative intensities greater than 10% of that of the base peak.

Comment on the mode of fragmentation of each sample and in terms of the expected spectra for other compounds of the same general type.

KNOWN COMPOUNDS:

Methanol

S. No

m/z value

Ion present

Possible loss of radical

1.

33

CH3OH+âˆ™ (C= 13)

2.

32 (molecular ion peak)

CH3OH+ (C= 12)

3.

31 (base peak)

CH2OH+

Hâ˙™

4.

30

CHO+ (C= 13)

H3â˙™

5.

29

CHO+ (C= 12)

H3â˙™

6.

15

CH3+

OHâ˙™

The molecular ion peak of methanol is 32 which represent the molecular weight of the compound. The base peak of the compound is 31. The molecular formula of the molecule is CH3OH.

The carbon atom has two isotopes, 13C and 12C. The 13C is less abundant and 12C is more abundant. With the help of mass spectrometer different isotopes of carbon can be identified as both the isotopes have different masses. The isotopic peaks for methanol were found at m/z value of 32, 33 and 29, 30. 32, 29 m/z value peaks represent the carbon with mass 12 and 33, 30 m/z value peaks represent the carbon with mass 13.

Loss of Hydrogen radical (1) from the molecular ion, CH3OH (32) produced CH2OH+ (31). Loss of H3 radical(3) from the molecular ion, CH3OH (32) produced CHO+ (29). Loss of OH radical(17) from the molecular ion, CH3OH (32) produced CH3+ (15). The same mode of fragmentation occurs in all the alcohols depending on the mass.

2. Propanone

S. No

m/z value

Ion present

Possible loss of radical

1.

58 (molecular ion peak)

CH3-CO-CH3+.

2.

43 (base peak)

CH3-CO+

CH3â˙™

3.

15

CH3+

CH3-COâ˙™

The molecular ion peak of propanone is 58 which represent the molecular weight of the compound. The base peak of the compound is 43. The molecular formula of propanone is C3H6O.

Usually, C-C bond is less strong than C-H bond and C-O bond. As a result cleavage occurs in the C-C bonds during the fragmentation in propanone. Loss of CH3 radical (15) from the molecular ion, CH3COCH3 (58) produced CH3CO+ (43). Loss of CH3CO radical (43) from the molecular ion, CH3COCH3(58) produced CH3+ (15). The same mode of fragmentation occurs in all the alcohols depending on the molecular formula.

3. Heptane

S. No

m/z value

Ion present

Possible loss of radical

1.

100 (molecular ion peak)

CH3-CH2-CH2-CH2-CH2-CH2-CH3+

2.

71

CH3-CH2-CH2-CH2-CH2+

CH3-CH2·

3.

57

CH3-CH2-CH2-CH2+

CH3-CH2-CH2·

4.

43 (base peak)

CH3-CH2-CH2+

CH3-CH2-CH2-CH2·

5.

29

CH3CH2+

CH3CH2CH2CH2CH2·

The molecular ion peak of heptane is 100 which represent the molecular weight of the molecule. The base peak of the compound is 43. The molecular formula of the compound is C7H16

Usually, C-C bonds are less stronger than the C-H bonds. So, in heptane fragmentation occured in the C-C bond, as a result of which alkyl cations and radicals are formed. The homologous series of alkyl cations are found at m/z values of 71, 57, 43, 29 and 15. Alkenylcarbocations are found at m/z values of 55, 41 and 27. These alkenylcarbocations are formed due to the loss of two hydrogen atoms. The same mode of fragmentation pattern will occur in all alkanes.

4. Dichloromethane

S. No

m/z value

Ion present

Possible loss of radical

1.

86

CH2Cl2+ (Cl = 37)

2.

84 (molecular ion peak)

CH2Cl2+ (Cl = 35)

3.

51

CH2Cl+

Cl·

4.

49(base peak)

CH2Cl+

Cl·

The molecular ion peak of dichloromethane is 84. The base peak of the compound is 49. The molecular formula of dichloromethane is CH2Cl2.

The chlorine atom has two isotopes each with different masses of 35amu (most abundant) and 37amu (less abundant). With the help of mass spectrometer different isotopes of chlorine can be identified, as both the isotopes have different masses. The isotopic peaks of chlorine were found at

m/z value of 86, 84 and 51, 49. 86, 51 m/z value peaks represent one of the chlorine with 37amu and 84, 49 m/z value peaks represent one of the chlorine with 35amu. The isotopic peaks of carbon was found at m/z value of 49, 50. 49 m/z value peak represent the carbon with atomic mass 12 and 50 m/z value peak represent the carbon with atomic mass 13.

Loss of chlorine radical (35) from the molecular ion, CH2Cl2 (84) produced CH2Cl+ (49). In the same way loss of chlorine (37) from the molecular ion, CH2Cl2 (86) produced CH2Cl+ (51). The same mode of fragmentation will occur in all alkyl halogens.

UNKNOWN COMPOUDS:

UNKNOWN 5

S. No

m/z value

Ion present

Possible loss of radical

1.

87

CH3CH2COCH2CH3+ (C= 13)

2.

86(molecular ion peak)

CH3CH2COCH2CH3+ (C= 12)

3.

57(base peak)

CH3CH2CO+

CH3CH2·

4.

29

CH3CH2+

CH3CH2CO·

The molecular ion peak of unknown 5 is 86 which represents the molecular weight of that compound. The base peak of the compound is at m/z value of 57. The molecular formula of the compound is C5H10O.

The carbon atom has two isotopes, 13C and 12C. The 13C is less abundant and 12C is more abundant. With the help of mass spectrometer different isotopes of carbon can be identified as both the isotopes have different masses. The isotopic peaks for unknown compound 5 were found at m/z value of 86, 87. 86 m/z value peaks represent the carbon with atomic mass 12 and 87 m/z value peak represent the carbon with atomic mass 13.

Loss of CH3CH2 radical (29) from the molecular ion, CH3CH2COCH2CH3 (86) produced CH3CH2CO+ (57). Loss of CH3CH2CO radical (57) from the molecular ion, CH3CH2COCH2CH3 (86) produced CH3CH2+ (29).

UNKNOWN 11

S. No

m/z value

Ion present

Possible loss of radical

1.

88 (molecular ion peak)

CH3CH2COOCH3+

2.

57

CH3CH2CO+

CH3Oâ˙™

3.

29 (base peak)

CHO+

C3H7Oâ˙™

4.

15

CH3+

C3H5O2âˆ™

The molecular ion peak of unknown 11 is 88, which represents the molecular weight of that compound. The base peak was found at the m/z value of 29. The molecular formula of the compound is C4H8O2.

Loss of CH3O radical (31) from the molecular ion, C4H8O2 (88) produced C3H5O+ (57). Loss Loss of C3H7O (59) from the molecular ion produced of CHO+ (29). Loss of C3H5O2 (73) from the molecular ion produced of CH3+ (15).

UNKNOWN 2

S. No

m/z value

Ion present

Possible loss of radical

1.

74(molecular ion peak)

CH3COOCH3+.

2.

43(base peak)

CH3CO+

CH3Oâˆ™

3.

15

CH3+

CH3COOâˆ™

The molecular ion peak of unknown compound 2 is 74, which represents the molecular weight of that compound. The base peak was found at the m/z value of 43. The molecular formula of the compound is C3H6O2

Loss of CH3O radical (31) from the molecular ion CH3COOCH3(74) produced CH3CO+ (43). Loss of CH3COO radical (59) from the molecular ion CH3COOCH3 (74) produced CH3+ (15).

Identify the unknowns with the aid of any additional information provided.

With the help of the mass spectrum the unknown compounds was identified as:

Unknown 5: 3-pentanone

Unknown 11: Methyl propionate

Unknown 2: Acetic acid methyl ester