



# **SPECTROSCOPY**

**Programme Code- MSCCH-17/18/19**

**Course Code-CHE- 504**

**Block – 3 Mass Spectrometry-II**

**Lecture-5**

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## ❖ *LEARNING OUTCOMES*

After studying this Chapter, you shall be able to:

❖ Know what is a molecular ion

❖ Learn about the fragmentation pattern and the factors affecting it

❖ Identify how fragments are generated

❖ Mass spectra of various compounds

## ❖INTRODUCTION:

The ionization of the sample molecule forms an entity known as a molecular ion that not only carries a net positive charge but also has an unpaired electron. This molecular ion entity then is actually a radical-cation and it contains which are odd in number. In a case where a molecular ion has a lifetime less than a few microseconds, it is not possible to observe it, as the timespan of its survival is too short. It is difficult to interpret a mass spectrum without a molecular ion peak as a reference. Although, it is fortunate that most organic compounds generally give a mass spectrum that includes a molecular ion peak. The organic compounds not giving a molecular ion peak in their mass spectrum respond successfully to the use of milder ionization conditions.

Aromatic rings, other conjugated pi-electron systems and cycloalkanes are amongst some of the simple organic compounds which are able to form the most stable molecular ions. Highly branched alkanes like alcohols, ethers and highly branched alkanes usually tend to show the greatest tendency toward fragmentation.

The molecular ion undergoes fragmentation in a mass instrument called the mass spectrophotometer. The fragments obtained from the mass instruments upon fragmentation and their nature give immense information about the molecular structure of the compound. For most of the compounds and their classes, the fragmentation is characteristic. Most compounds and their various classes have a characteristic fragmentation pattern.

## ❖ Factors for Fragmentation:

- a) Energy of the molecular ion and the fragments formed from it
- b) Stability of the bonds in the ions
- c) For rearrangements: steric factors, It is easier to move a H atom than a whole group
- d) Stability of the formed ions or neutral particles resonance stabilization such as in an acylium ion.

## ➤ Stevenson's rule :

When fragment ions form in the mass spectrometer, they almost always do so by means of unimolecular processes. These processes that are energetically most favourable give rise to the most fragment ions. The important postulate of the Stevenson's rule is that the most probable

fragmentation is the one that leaves positive charge on the fragment with the lowest ionization energy. In other words, fragmentation processes that lead to the formation of more stable ions are favoured over processes that lead to less stable ions.

❖ **Types of Fragmentation:** Various types of Fragmentation are given as follow:

1. Sigma electron ionisation
2. Radical site initiation
3. Charge site initiation
4. Rearrangement

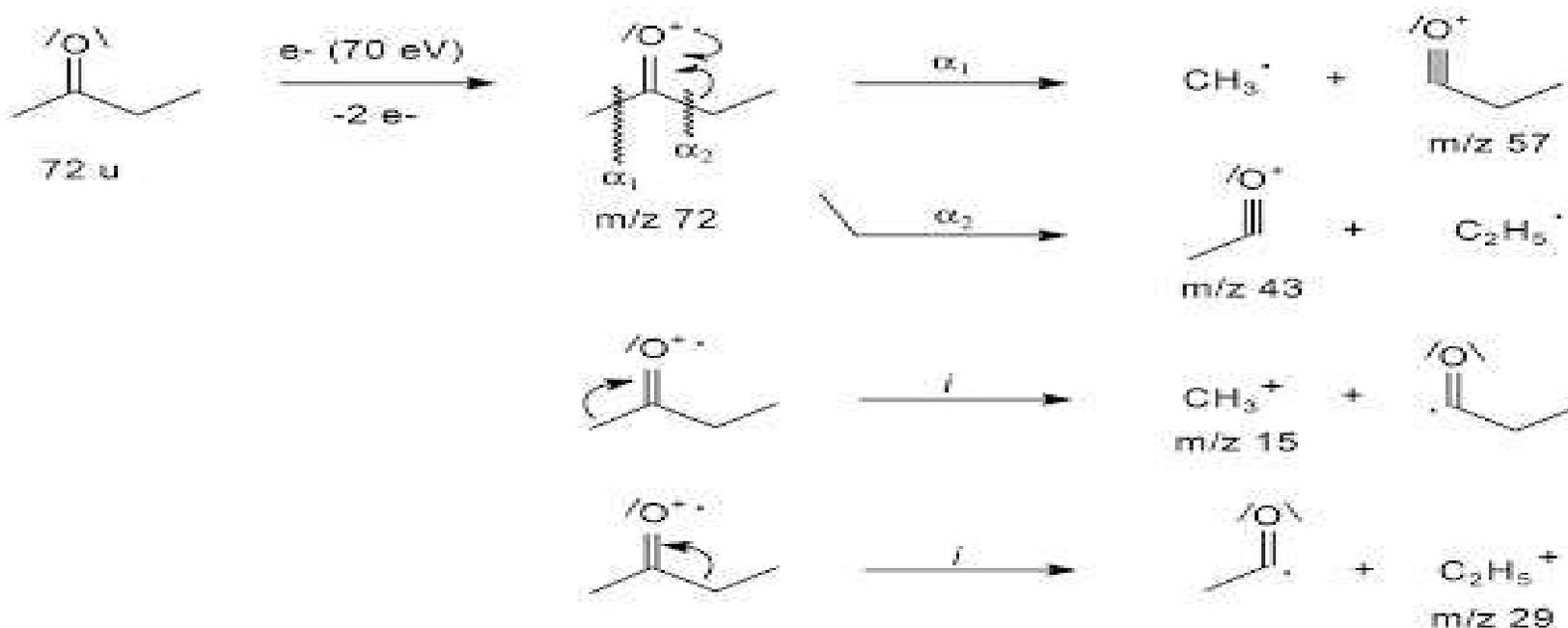
# 1. Sigma electron ionisation

The fragmentation in molecular ion of alkane takes place as follows:



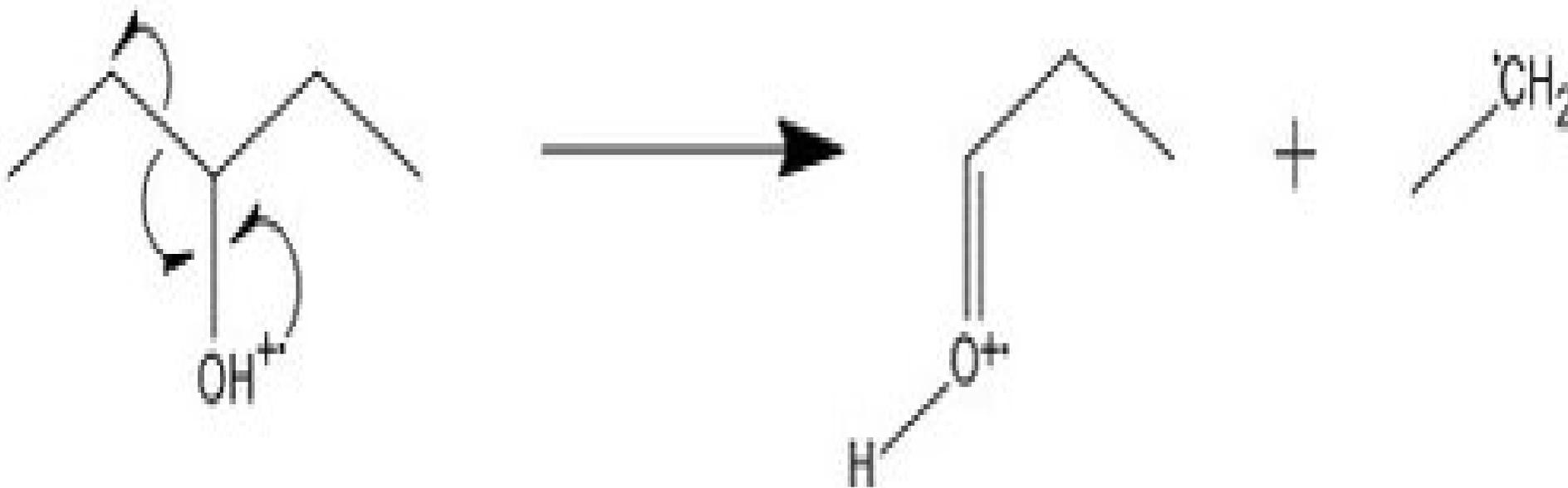
**Example:** Homolytic dissociation in 2-butanone. The acylium ion formed by loss of the largest alkyl radical is preferred.

Butanone Molecule    Ionization    Butanone Molecular Ion    Fragmentation    Fragment Ions and Radicals



## 2. Radical site initiation:

In some molecular ions, fragmentation occurs by donation of an electron to form a new bond to an adjacent atom concomitant with cleavage of another bond to that atom. Radical-site-initiated fragmentation is one of the most common one-bond cleavages and is more commonly called an  $\alpha$ -cleavage.  $\alpha$ -cleavages may occur at saturated or unsaturated sites that may or may not involve a heteroatom.



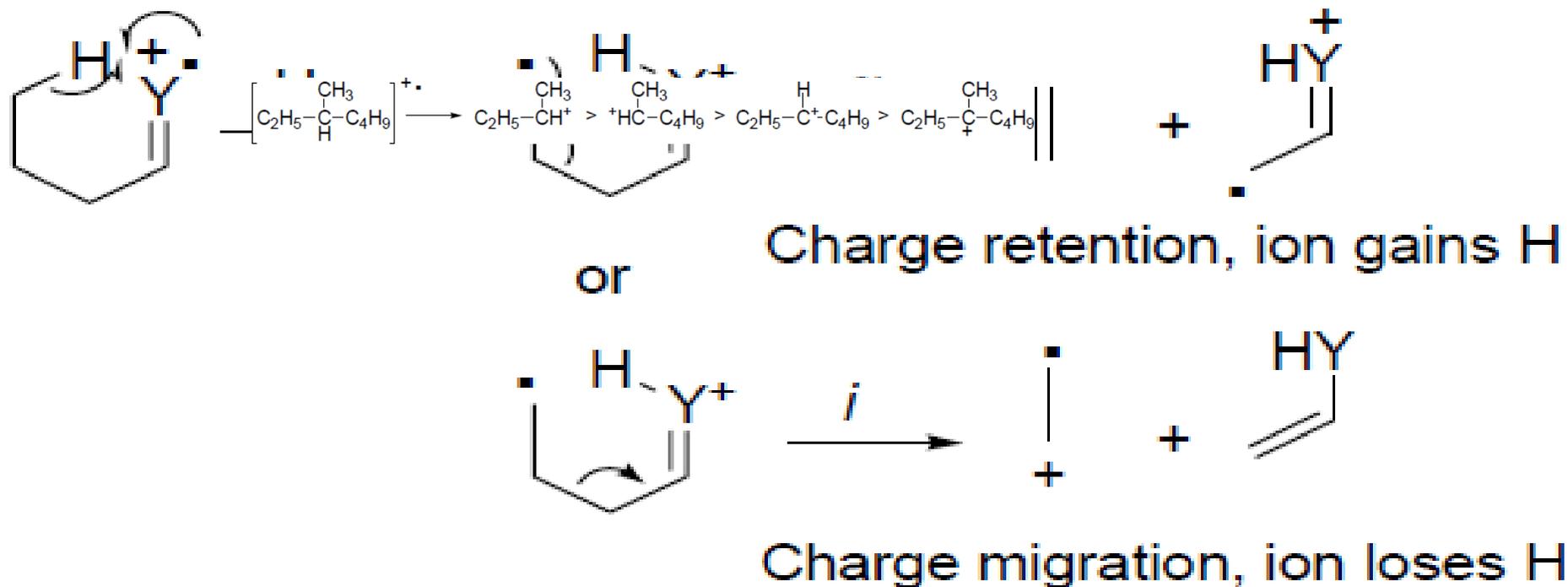
### 3. Charge site initiation

This charge-site initiated or inductive cleavage is often indicated in a fragmentation mechanism by the symbol *i*. This involves the attraction of an electron pair by an electronegative heteroatom that ends up as a radical or as a closed-shell neutral molecule. When  $\alpha$ -cleavage is a fragmentation of  $OE^+$  only, inductive cleavage can operate on either an  $OE^+$  or an  $EE^+$ .

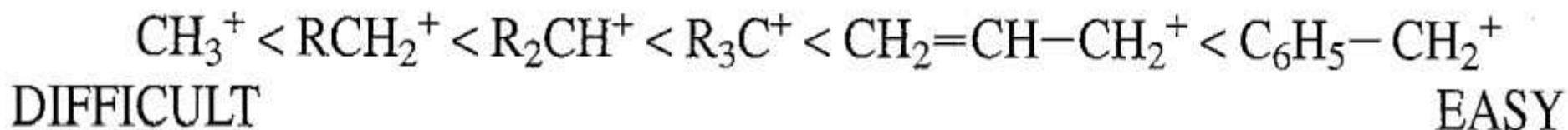


## 4. McLafferty Rearrangements :

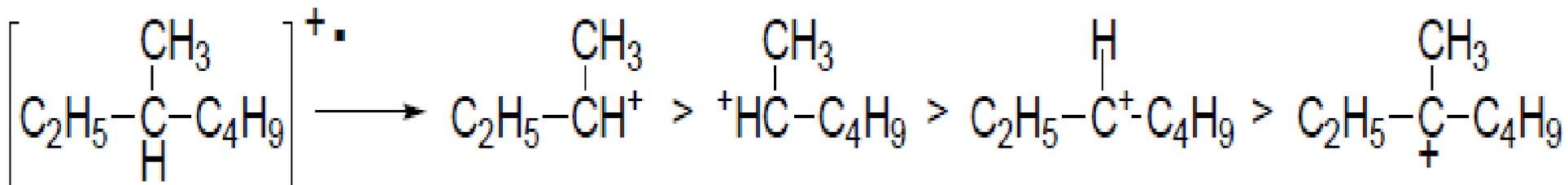
This was first described by Fred Mc Lafferty in 1956 and is one of the most predictable fragmentations, next to the simple  $\alpha$ -cleavage. In this process, a hydrogen atom on a carbon 3 away from the radical cation of an alkene, arene, carbonyl, or imine (a so called  $\gamma$ -hydrogen) is transferred to the charge site via a six membered transition state, with concurrent cleavage of a sigma bond between what were the original  $\beta$  and  $\gamma$  carbons. For simplicity, the mechanism of the McLafferty rearrangement is usually drawn as a concerted process.



Cleavages which forms the carbocation which is more stable are favored. Thus ease of fragmentation to form ions increases in the order.



In branched radical cations, the largest group is preferentially lost.

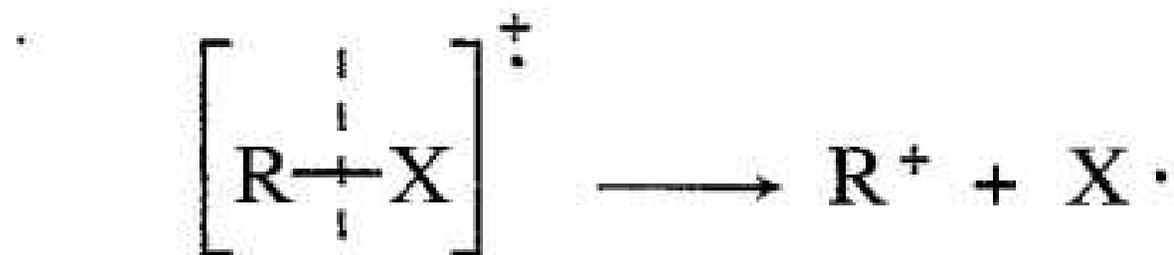
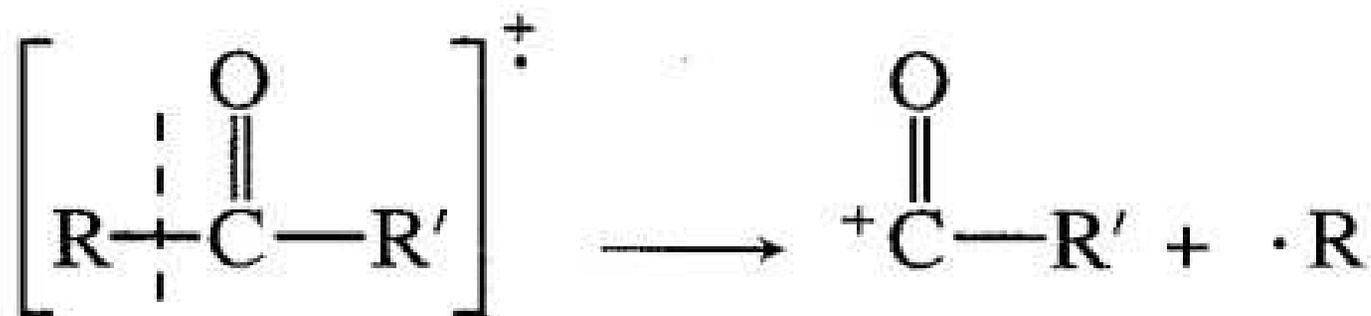


## One bond or two bond cleavages

Fragmentation may involve one bond or two bond cleavage. One of the most well-known modes of fragmentation involves the cleavage of one bond. This process yields an odd electron neutral.

fragment and an even-electron fragment ion generated from odd electron molecular ion. The neutral fragment that is lost is radical and the ionic fragment is the carbocation type.

Example of fragmentation via the **cleavage of one of the bonds are:**

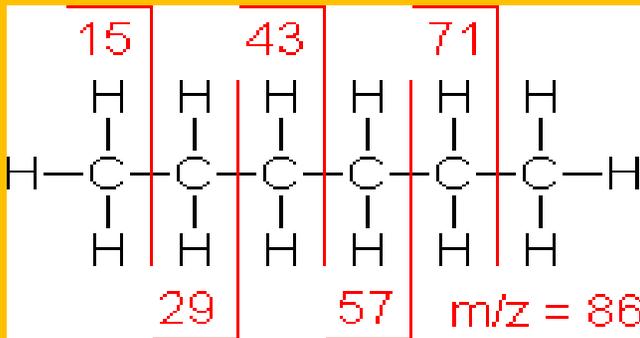
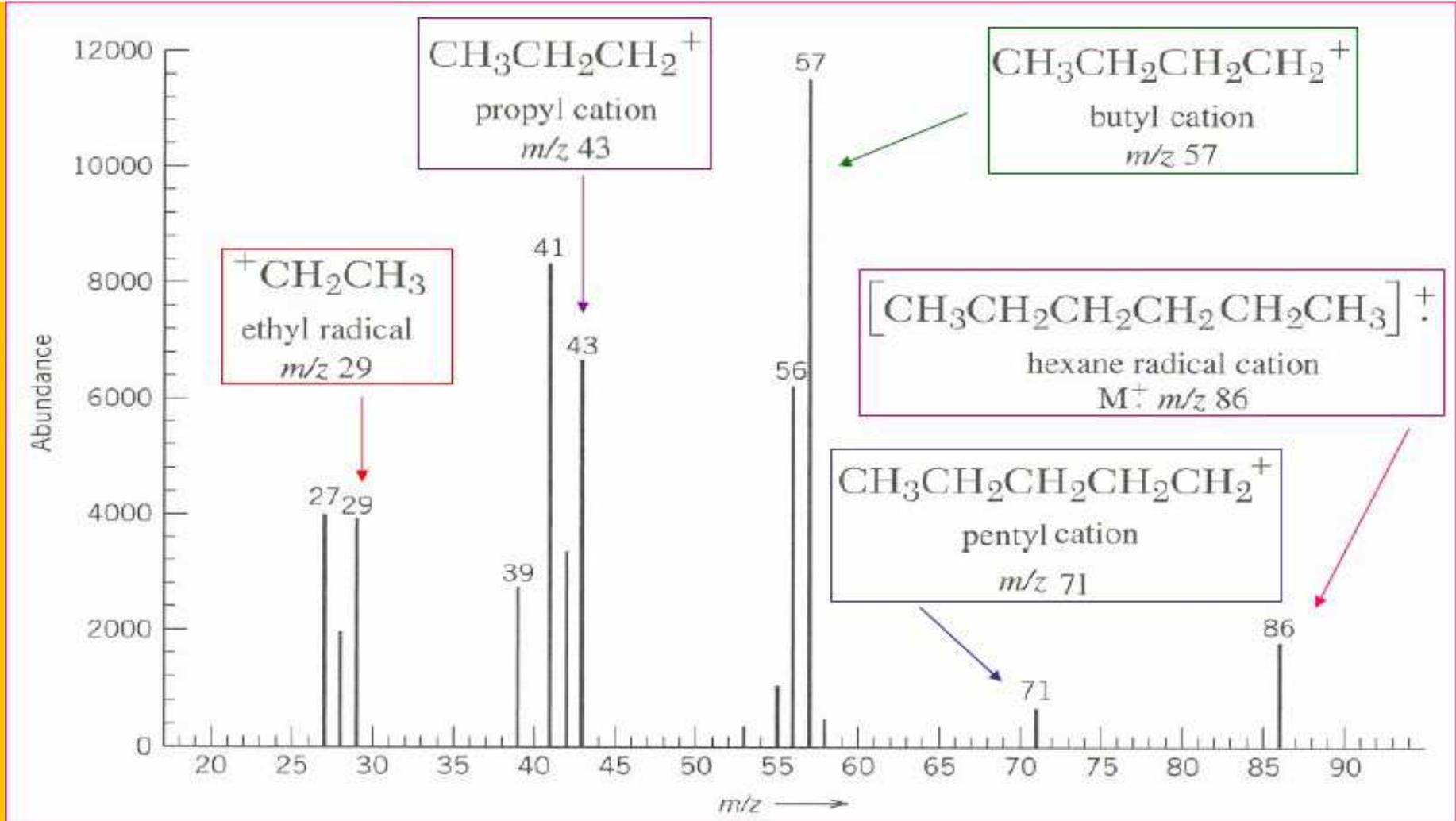


$\text{X} = \text{halogen, OR, SR, or NR}_2$   
 where  $\text{R} = \text{H, alkyl, or aryl}$

## ❖ Fragmentation Pattern of some Compounds:

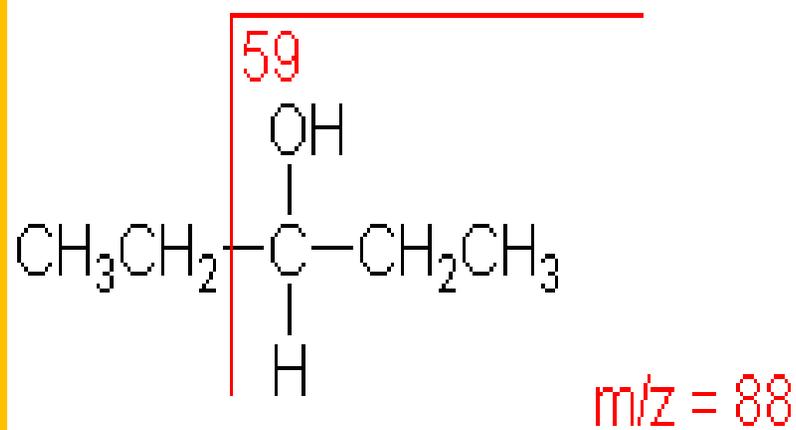
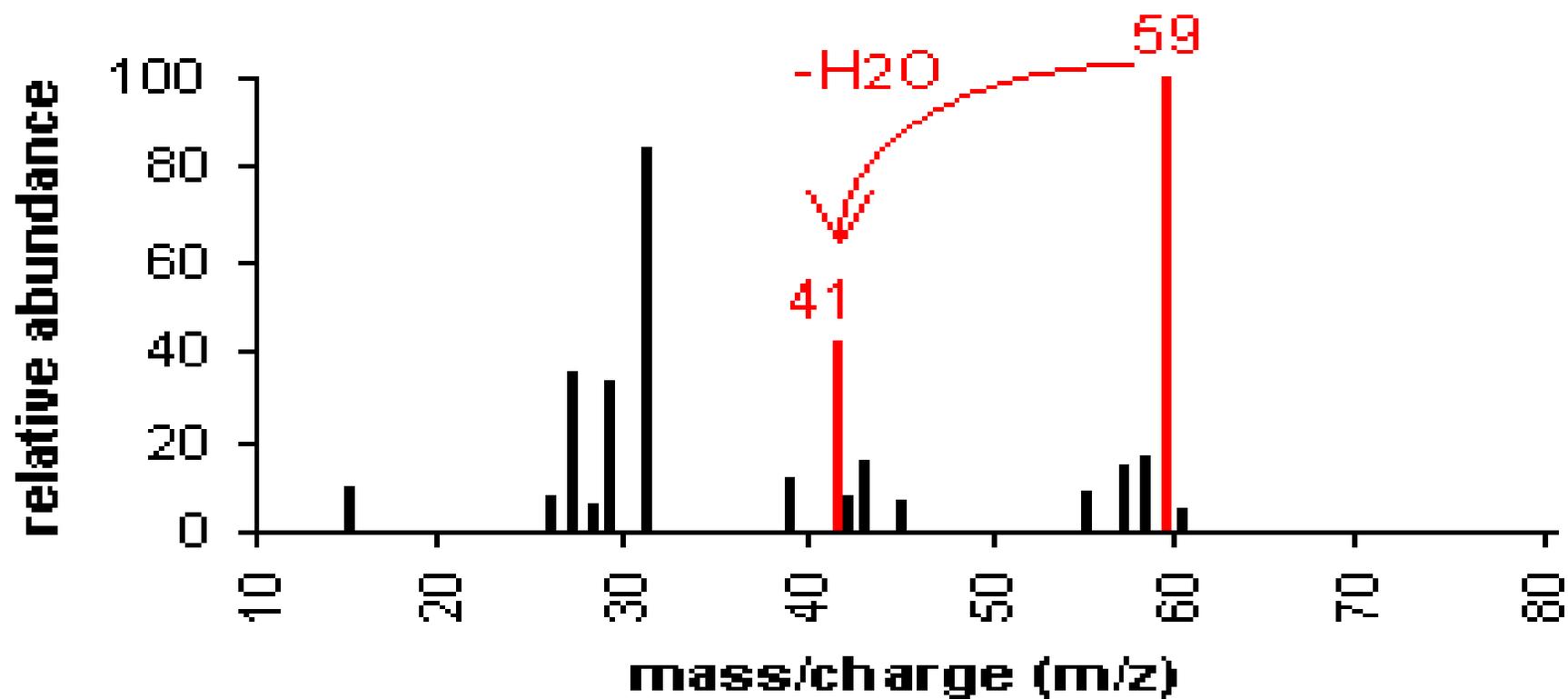
### 1. Fragmentation in Alkanes:

Alkanes are characterized by strong molecular ion peaks. The fragmentation pattern contains clusters of peaks 14 mass units apart (which represent loss of  $(\text{CH}_2)_n\text{CH}_3$ ). As the carbon skeleton becomes more highly branched, the intensity of the molecular ion peak decreases. Straight chain alkanes have fragments that are always primary carbocations. As seen in the mass spectra of hexane ( $\text{C}_6\text{H}_{14}$ ) with MW = 86.18 in given below figure 1.



## 2. Fragmentation in 3-pentanol:

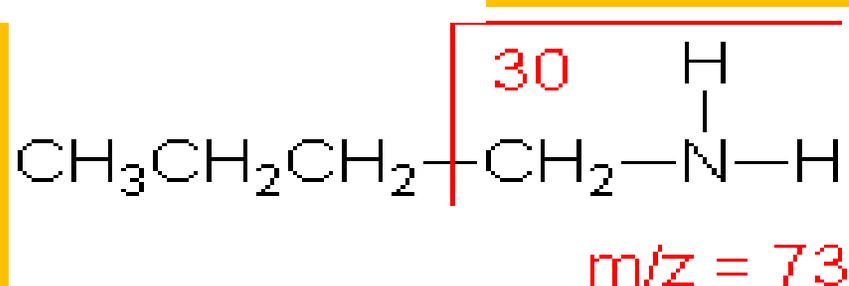
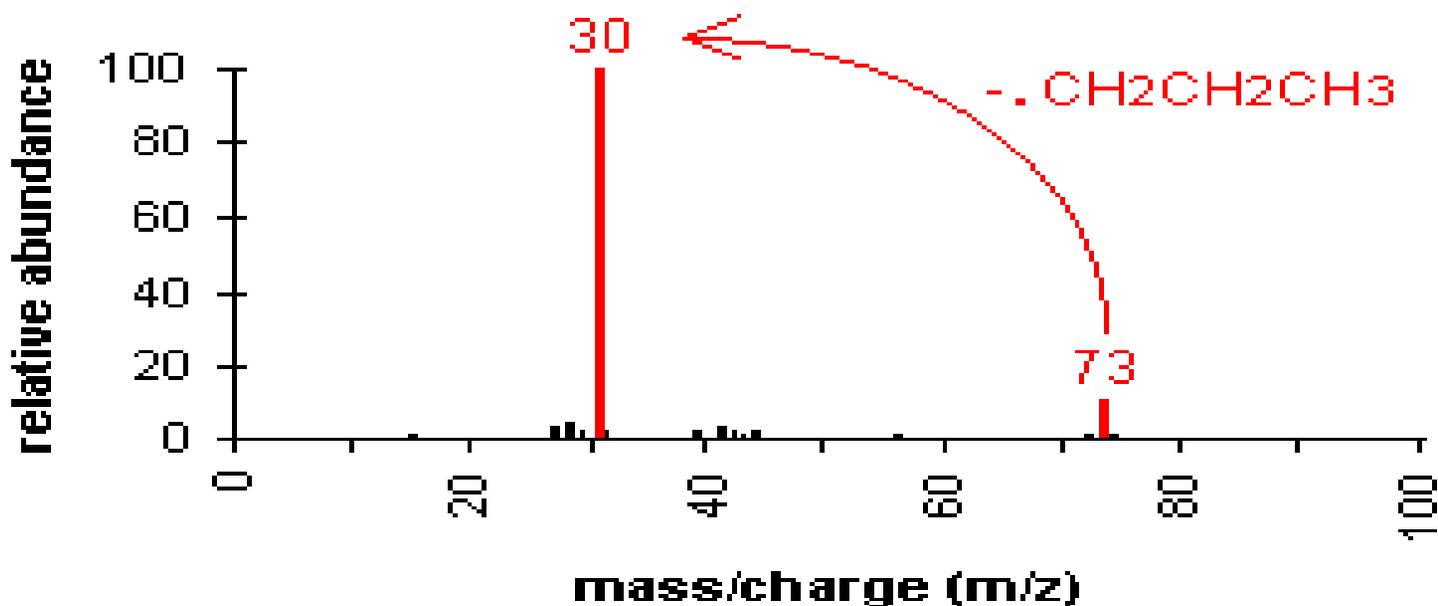
A functional group having a heteroatom Y containing non-bonding valence electrons (Y=N, O, S, X etc.) drastically affects the pattern of fragmentation of a compound. The intensity of the molecular ion peak in the mass spectrum of a primary or a secondary alcohol is usually rather low, and the molecular ion peak is often entirely absent in the mass spectrum of a tertiary alcohol. Cleavage of the C-C bond adjacent to the oxygen usually occurs. A loss of H<sub>2</sub>O may occur as seen in the spectra of 3-pentanol (C<sub>5</sub>H<sub>12</sub>O) with MW = 88.15 in given below figure 2.



### 3. Fragmentation in aliphatic amines :

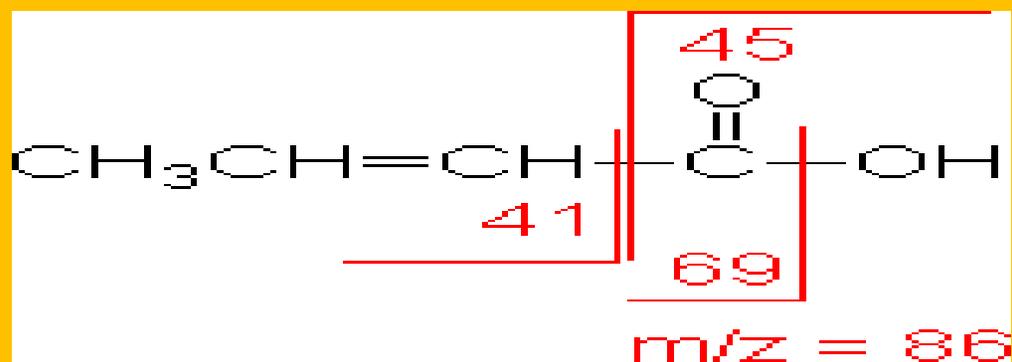
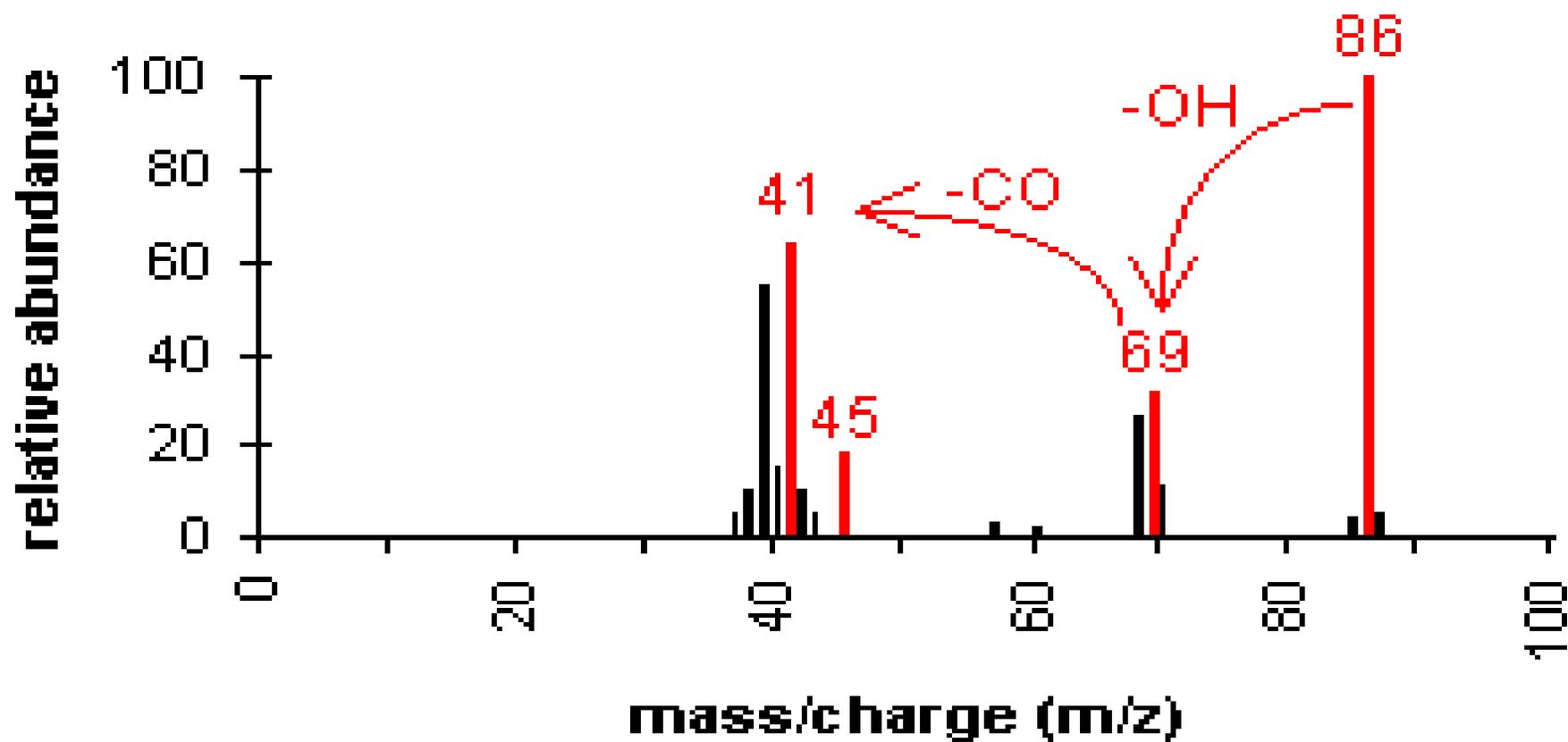
In case of aliphatic amines molecular ion peak maybe very weak or maybe totally absent.  $\alpha$ -cleavage dominates aliphatic amines.

Fragmentation pattern of n-Butylamine ( $C_4H_{11}N$ ) with MW = 73.13 is shown in below figure 3.



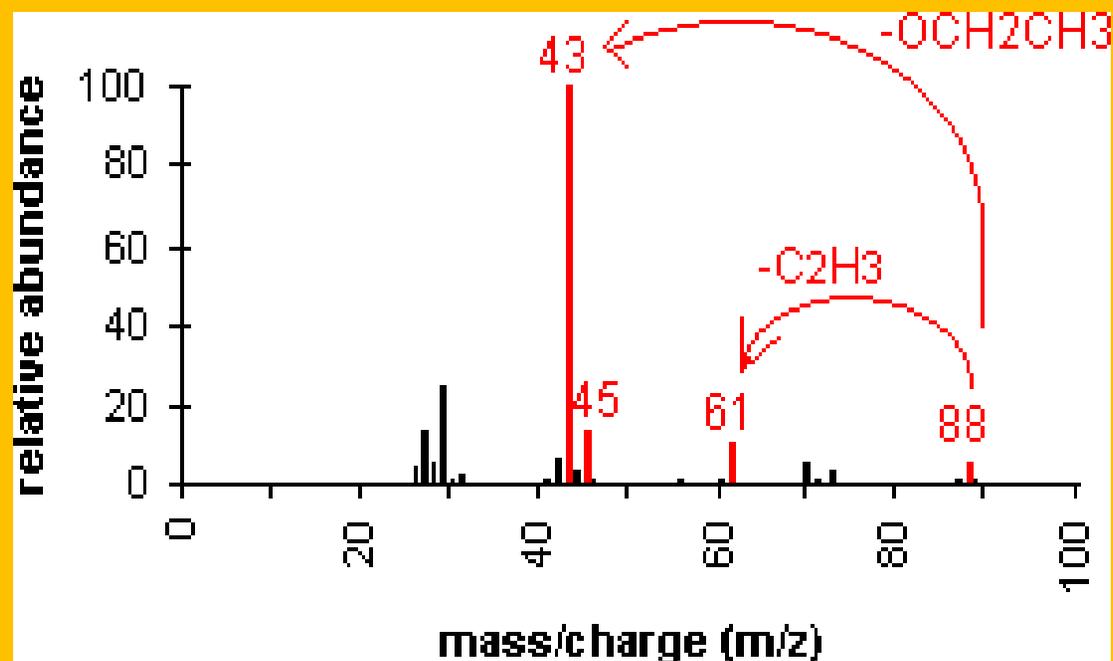
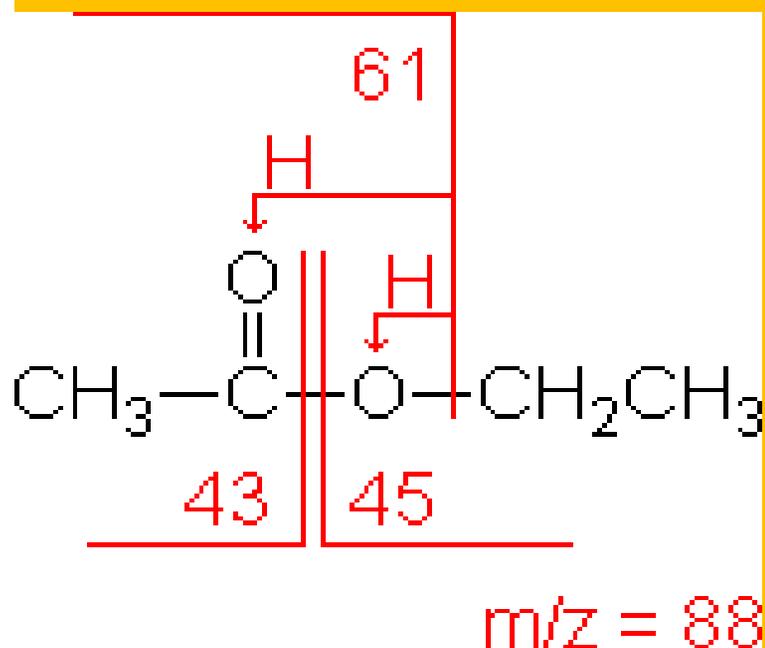
### **3. Fragmentation in Aliphatic carboxylic acids :**

Aliphatic carboxylic acids generally show weak but observable, molecular peaks. Aromatic carboxylic acids on the other hand show strong molecular ion peaks. In short chain acids, peaks due to the loss of OH (molecular ion less 17) and COOH (molecular ion less 45) are prominent due to cleavage of bonds next to C=O. The mass spectra of 2-butenoic acid (C<sub>4</sub>H<sub>6</sub>O<sub>2</sub>) with MW = 86.09 is shown in given figure 4.



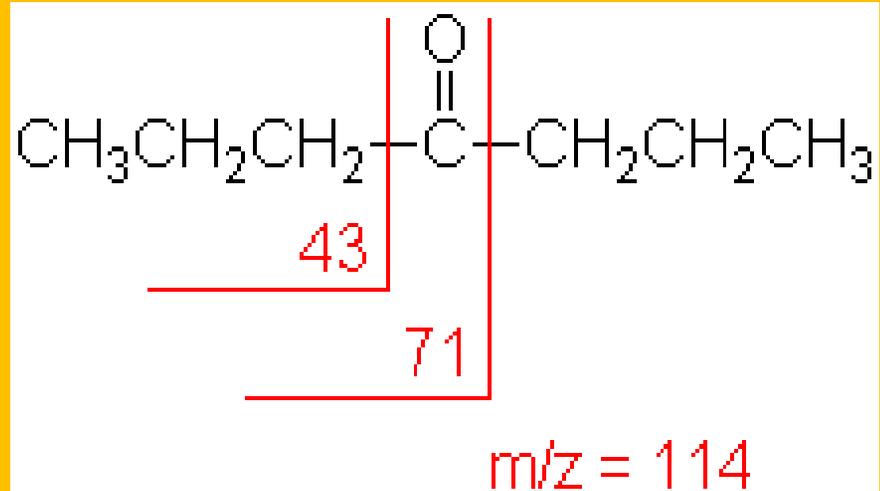
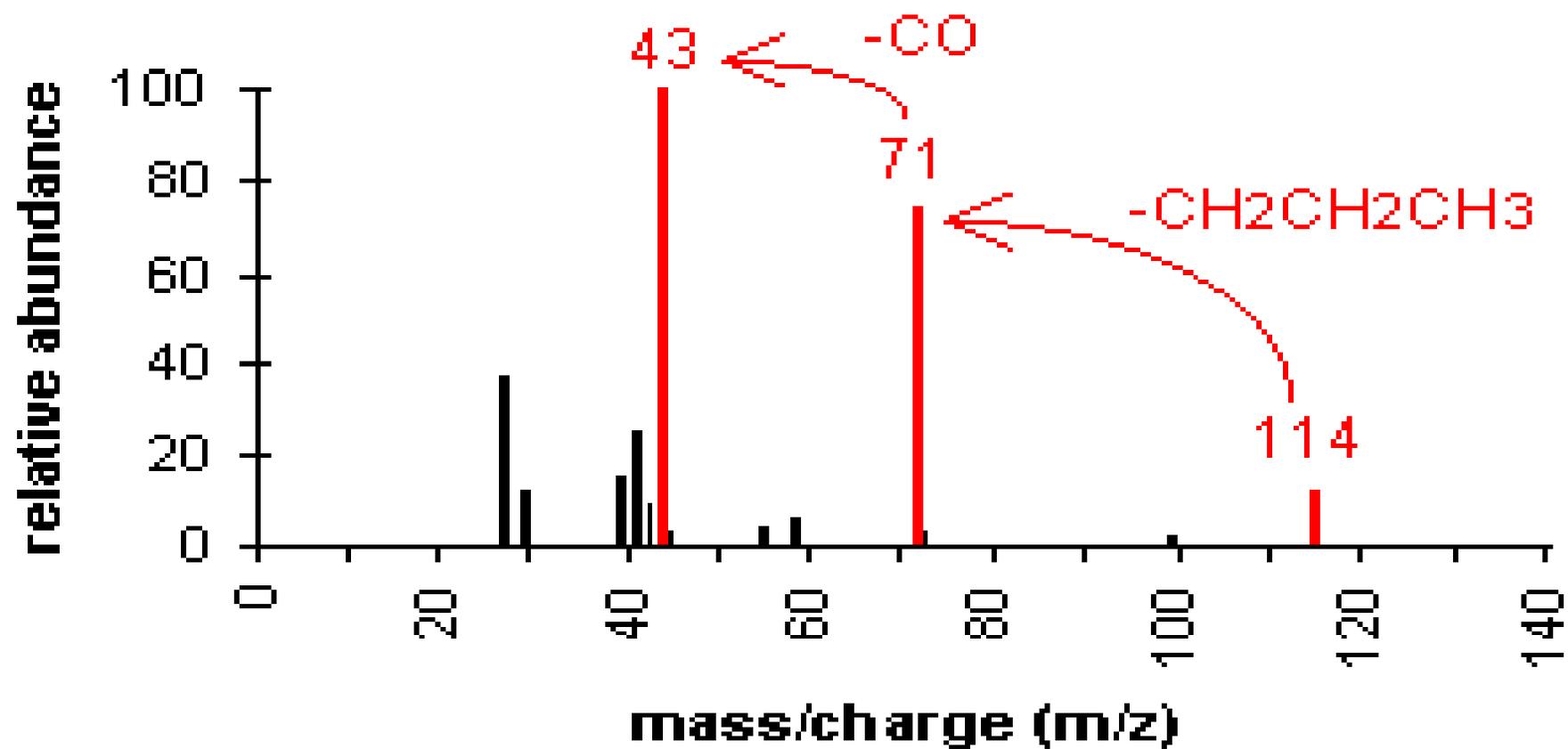
## 4. Fragmentation in esters:

Fragmentation in esters is especially facile, but it is usually possible to observe weak molecular ion peaks in the mass spectra of methyl esters. The esters of higher alcohols form much weaker molecular ion peaks, and esters of alcohols larger than four carbon atoms may form molecular ion peaks that fragment too quickly to be observed. In esters fragments appear due to bond cleavage next to C=O (alkoxy group loss, -OR) and hydrogen rearrangements as can be seen in the mass spectra of ethyl acetate ( $C_4H_8O_2$ ) with MW = 88.11 (figure 5).



## 5. Fragmentation in ketone:

The mass spectra of ketones show an intense molecular ion peak. In case of ketones major fragmentation peaks result from cleavage of the C-C bonds adjacent to the carbonyl. The pattern of fragmentation is similar to that of aldehydes as briefly described above. Stevenson's rule is to be kept in mind while considering the cleavage of alkyl groups. Generally acylium ion is formed by  $\alpha$ -cleavage in ketones and in aldehydes. In case of 4-Heptanone ( $C_7H_{14}O$ ) with MW = 114.19 fragments appear at m/z 71 and 43 (figure 6).



THANK YOU