

3. Ionisation and Ion Sources

In this part of the unit you will encounter a detailed treatment of the phenomenon of ionisation. We will begin with a discussion of electron impact ionisation which encompasses the advantages and disadvantages of the method. Alternative methods of ionisation are also discussed. These are chemical ionisation, field ionisation, field desorption and fast atom bombardment. In each case, advantages and disadvantages are highlighted.

3.1. IONISATION BY ELECTRON IMPACT

We have already dealt, briefly, with ionisation of molecules in Part 1. Let us now look at this aspect in more detail. Firstly, we will concentrate on the method of ionisation we have already discussed; electron impact (EI). We will look at its advantages and shortcomings and then go on to examine alternative methods of ionisation.

As we discussed earlier, when electrons pass through or very near to a molecule, they can bring about its ionisation. Usually this process results in formation of positive ions, but electron attachment and hence negative ion formation is also possible. The probability of electron capture is about 100 times less than that of electron removal and, furthermore, when a moving electron is taken up by a molecule, the translational energy of the electron must be taken up by the

molecular ion (M^-). This translational energy is usually converted into vibrational energy.

- Π What might you expect to happen to such a negative molecular ion with a high degree of vibrational energy?

The molecular ion would be expected to fragment very readily. Thus negative fragment ions are observed, but it is relatively uncommon to observe negative molecular ions. Furthermore, the fragment ions are often not very informative. For example, if the molecule contains a nitro group, the spectrum is dominated by the ion, NO_2^- and there are few other ions giving any structural information.

SAQ 3.1a

Can you think of other groups or atoms commonly encountered in organic chemistry which would also be likely to dominate the negative ion spectra of molecules of which they are part? On what basis did you make your choice?

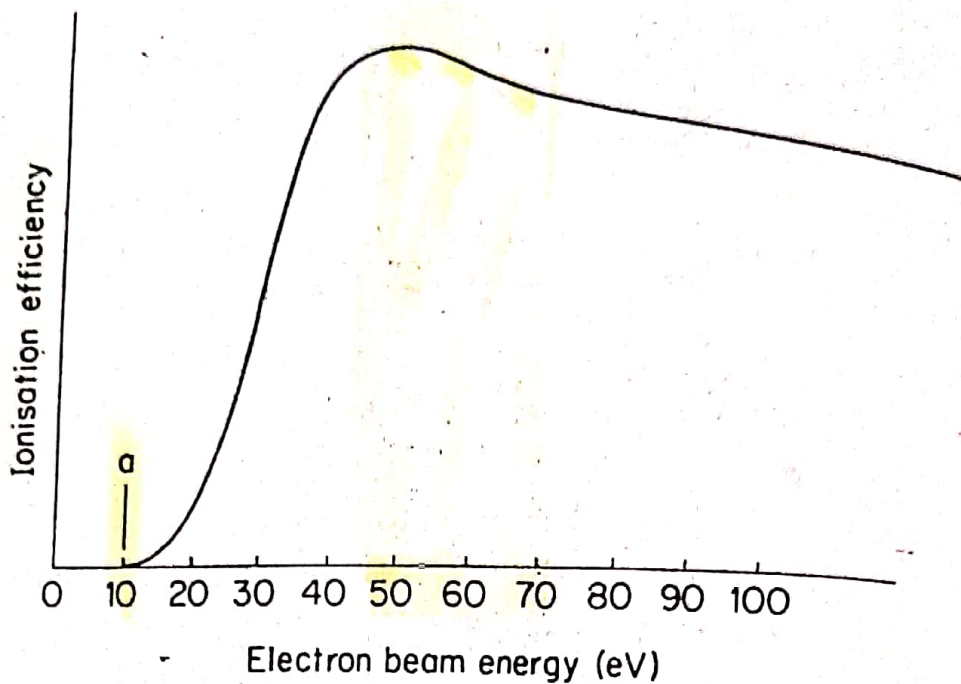


Fig. 3.1a. A typical ionisation efficiency curve

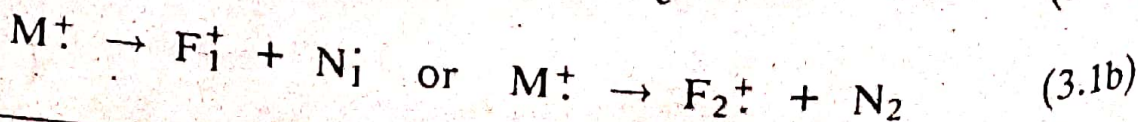
The point marked (a) on the curve corresponds to the first appearance of ions as the electron beam energy is increased.

□ What is the beam energy value at point (a) known as?

It is known as the *ionisation potential* and this applies to the process in Eq. 3.1a



Thus, in principle, mass spectrometry can be used to measure ionisation potentials. In practice, there are experimental difficulties in making such measurements and thus the results are not terribly accurate. If the ionisation efficiency curve for a fragment ion is examined, then a similar parameter can be measured. This is known as the *appearance potential* and corresponds to the overall energy for the two processes given in Eq. 3.1a and Eq. 3.1b



Information gained from ionisation and appearance potential measurements can be used to determine thermodynamic quantities such as the heats of formation of ions and bond dissociation energies. However, further discussion of this aspect is outside the scope of this programme and the interested reader is referred to the textbooks by Williams and Howe and Rose and Johnstone listed in the bibliography for a more detailed coverage.

If we look again at Fig. 3.1a, we can see that the number of ions formed increases dramatically as the beam energy is increased from the ionisation potential to about 50 eV. It then reaches a virtually constant value.

II Explain why the shape of the curve helps you to understand earlier comments that mass spectra are usually recorded using 50–70 eV bombarding electrons with preference being given to the higher value.

In order for the spectrometer to operate at maximum sensitivity, we require the maximum yield of ions from any given amount of sample. The curve shows we would get this at approximately 50 eV. However, at that value we are very close to the steeply increasing part of the curve and thus any small unintentional experimental decrease in beam energy would lead to a dramatic reduction in ionisation efficiency. If we increase the operational beam energy to 70 eV, we sacrifice only a small amount in ionisation efficiency, but move well into the plateau region, where small changes in beam energy have little effect on ionisation efficiency. For this reason electron impact mass spectra are usually recorded at 70 eV.

II There is a further reason for recording mass spectra at energies well above the ionisation potential. This was discussed in Part 1. Can you recall what it was?

(A spectrum recorded with a beam energy set at or about the value of the ionisation potential will show the presence of only molecular ions. Fragmentation only becomes important at higher beam energies. The spectra of C_6H_5COOH recorded at 9, 12, 15, 20, 30 and 70 eV are shown in Fig. 3.1b.

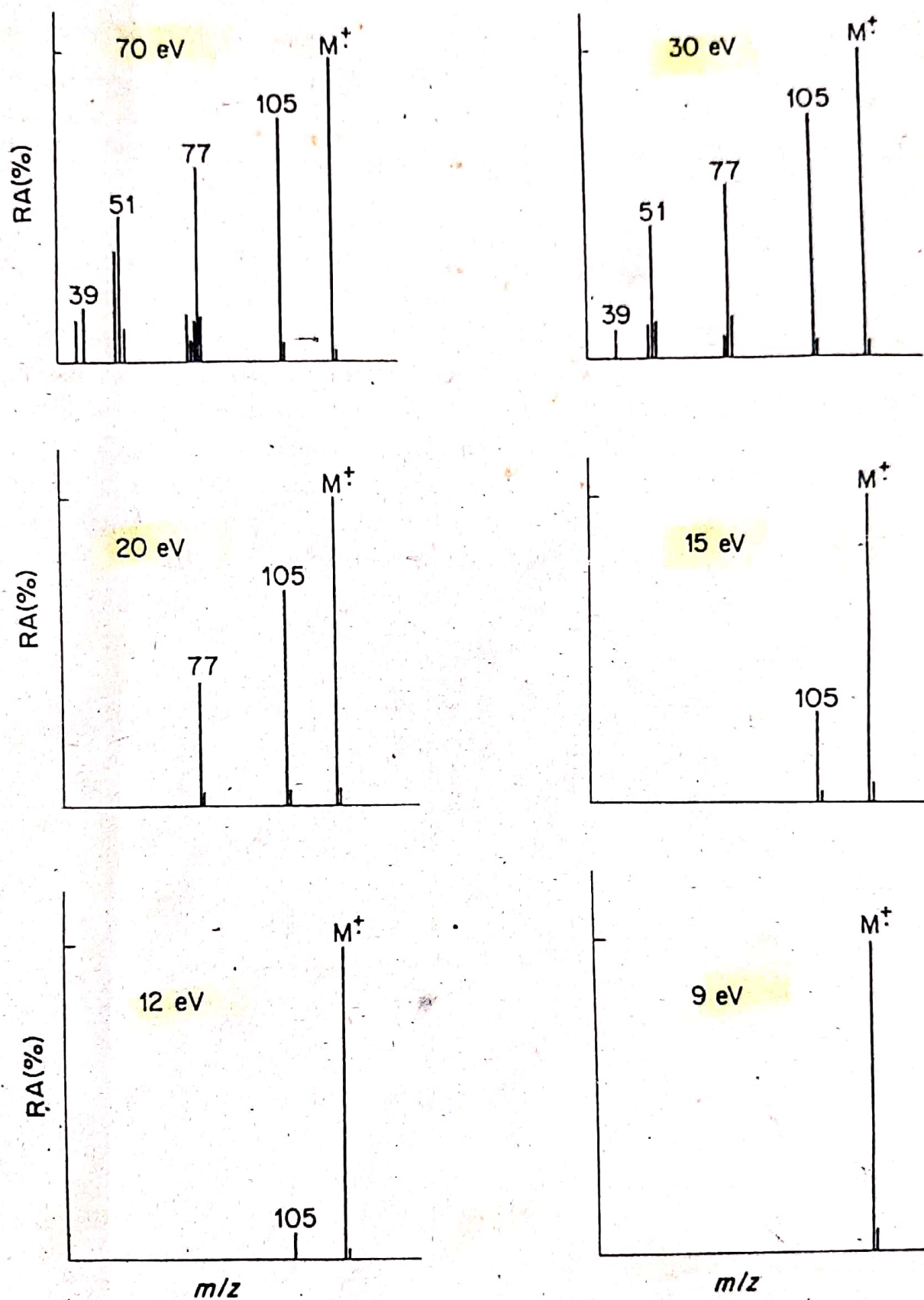


Fig. 3.1b. Mass spectrum of C_6H_5COOH using different beam energies

Maximum production of fragment ions is not observed until one employs the higher values, although the predominant fragmentation, which occurs with low energy requirements is seen at 12 eV. Usually most structural information is gained when the maximum number of fragment ions are produced.)

It should, however, be pointed out that for very complex molecules, many of the low mass ions will not be structurally informative and may in fact conceal the presence of the most important ions, so that it is often worth recording a low voltage spectrum. This is illustrated by the spectra of *genipin* (Fig. 3.1c) recorded at (a) 70 eV and (b) 10 eV. It is the case that m/z 78 and m/z 96 are both significant ions in elucidating the structure of this molecule. At 70 eV, m/z 96 does not look particularly significant and may be overlooked amongst the plethora of other ions between m/z 60 and m/z 100.

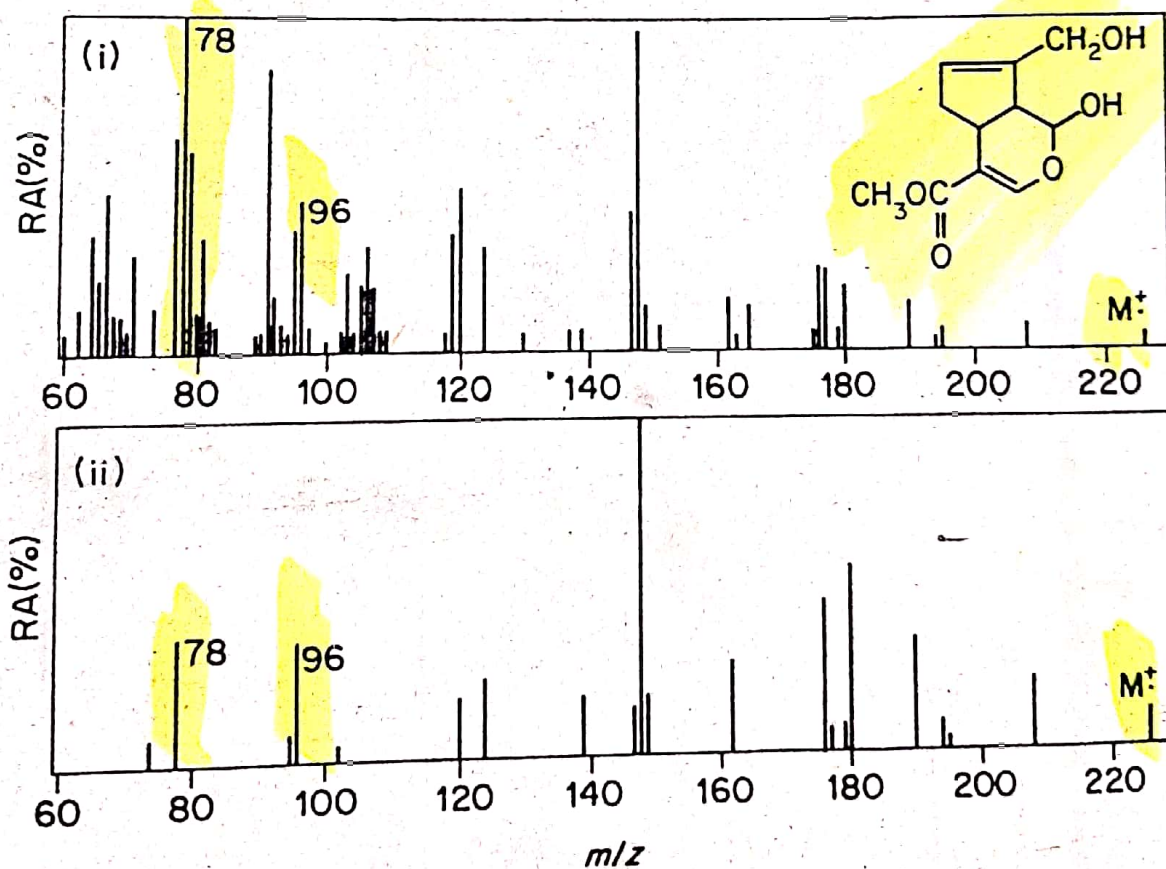


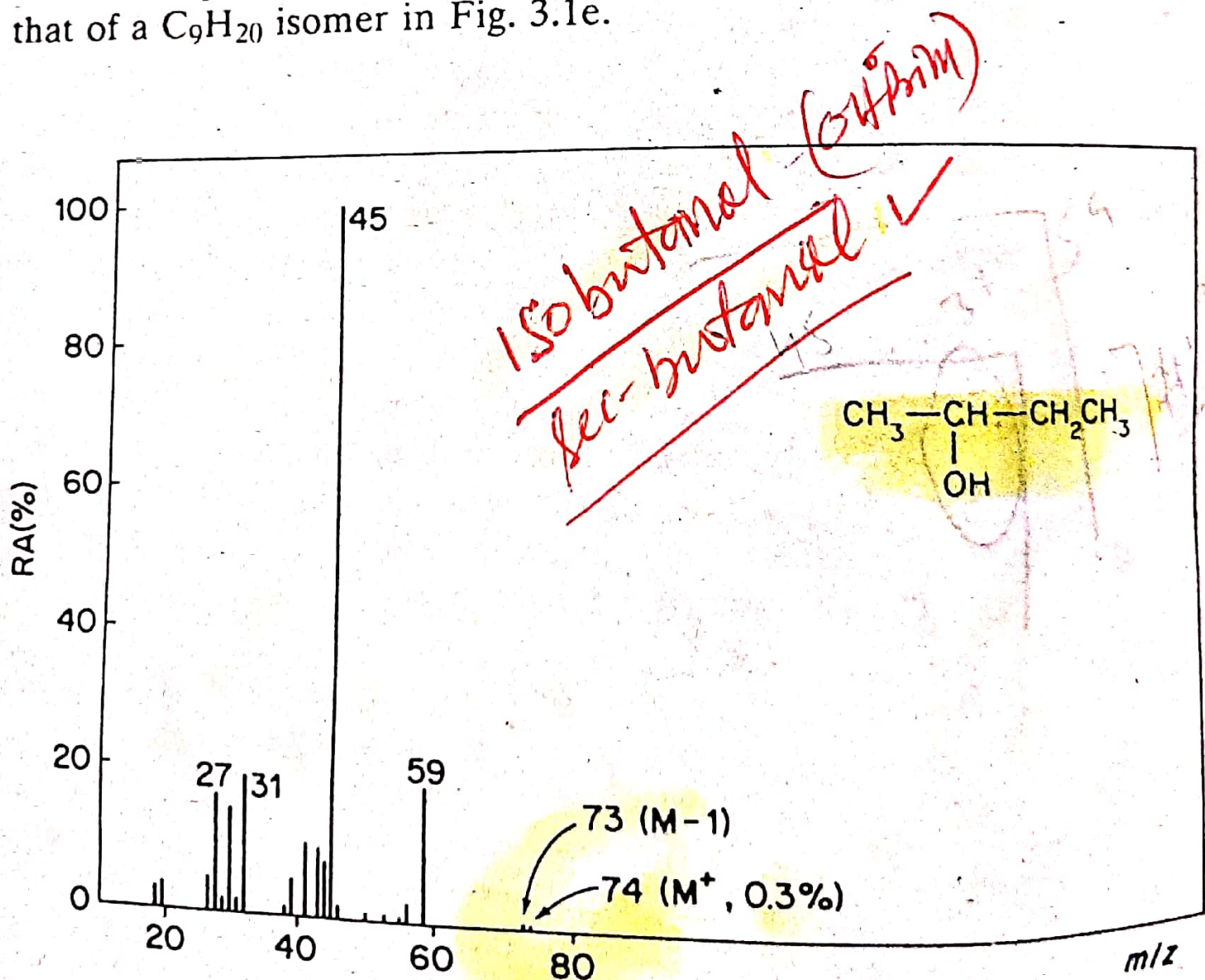
Fig. 3.1c. Mass spectrum of genipin at (i) 70 eV and (ii) 10 eV

The low voltage spectrum clearly reduces this complexity without losing the important ions.

Electron impact ionisation is the most widely used method of ionisation in mass spectrometry. This is because for most molecules it produces both molecular and fragment ions. Thus, it allows determination of both relative molecular mass and molecular structure for such molecules. You will learn about interpreting such spectra later.

In some cases, however, there are problems with electron impact spectra. This is illustrated with some examples.

The mass spectra of $C_2H_5CH(CH_3)OH$ is shown in Fig. 3.1d and that of a C_9H_{20} isomer in Fig. 3.1e.



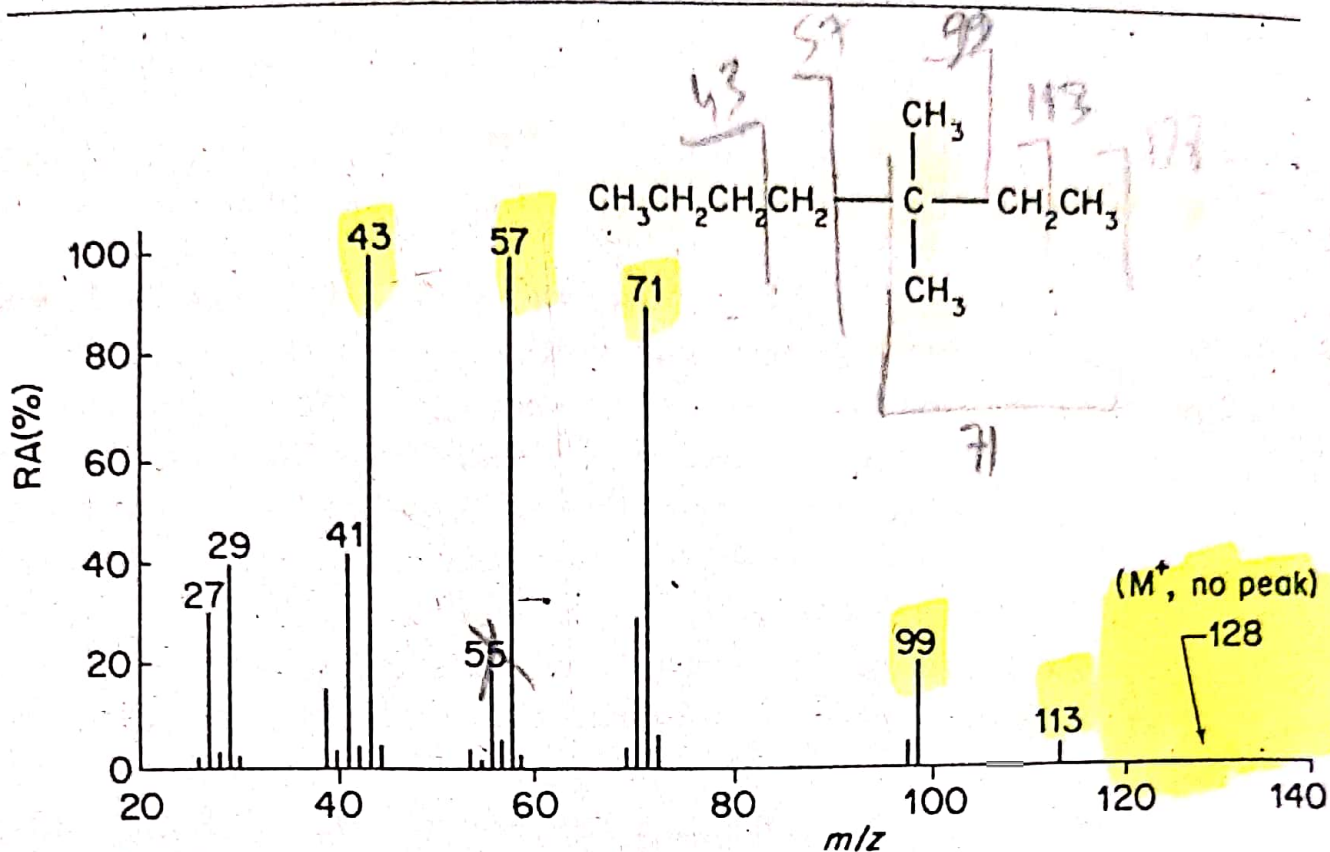
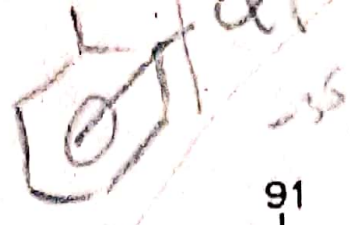


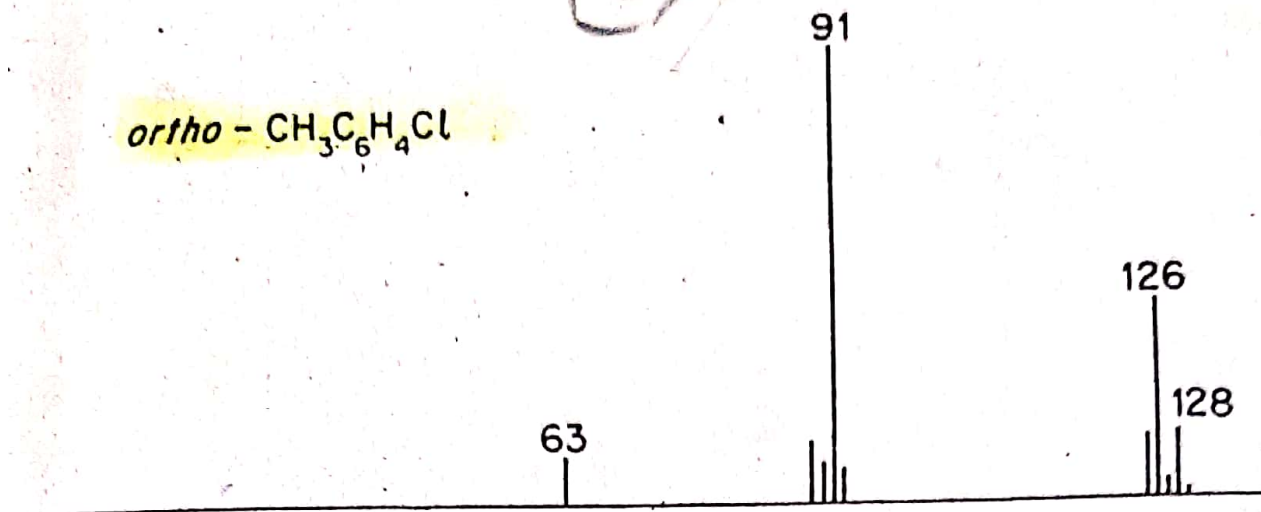
Fig. 3.1e. Mass spectrum of C_9H_{20}

The molecular ion of $C_2H_5CH(CH_3)OH$ is of very low relative abundance and that of C_9H_{20} is not observed. This occurs because both molecules are very susceptible to fragmentation. There are a considerable number of molecules of this type for which all or almost all the molecular ions formed fragment before they leave the ion source. For these types of molecule it is difficult to determine their relative molecular mass.

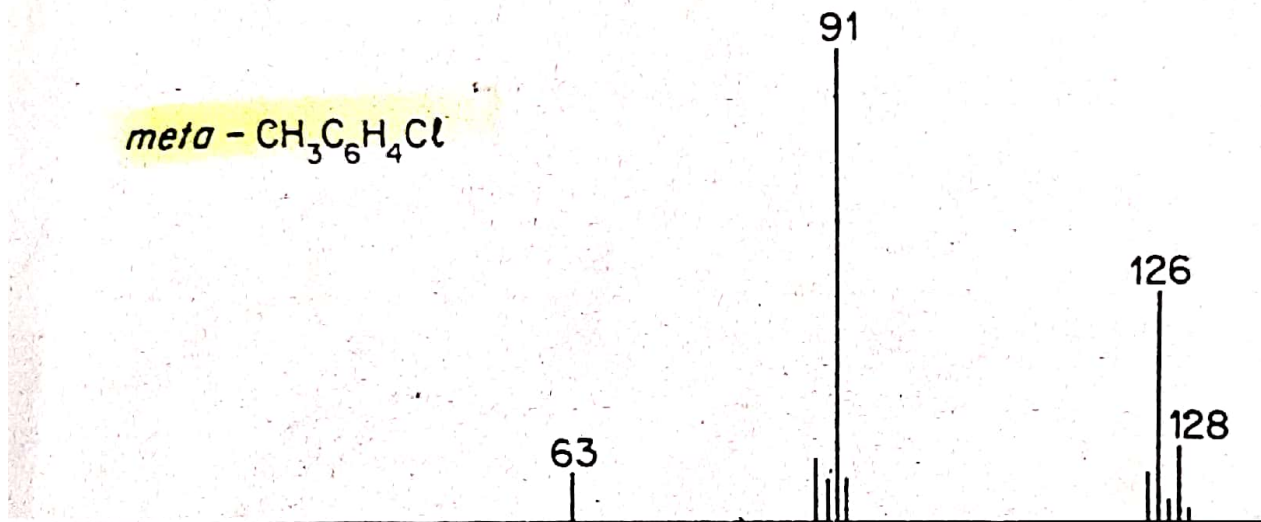
II The spectra shown in Fig. 3.1f, 3.1g and 3.1h illustrate the three other shortcomings of electron impact ionisation. Can you work out what the problems are in each case?



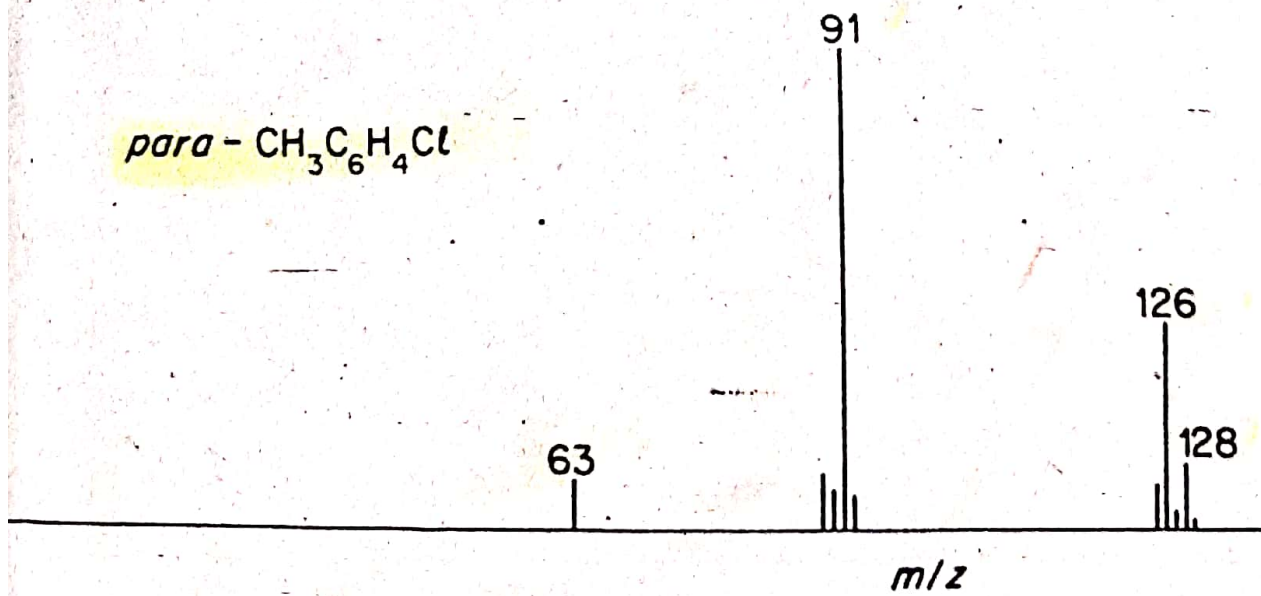
ortho - $\text{CH}_3\text{C}_6\text{H}_4\text{Cl}$



meta - $\text{CH}_3\text{C}_6\text{H}_4\text{Cl}$



para - $\text{CH}_3\text{C}_6\text{H}_4\text{Cl}$



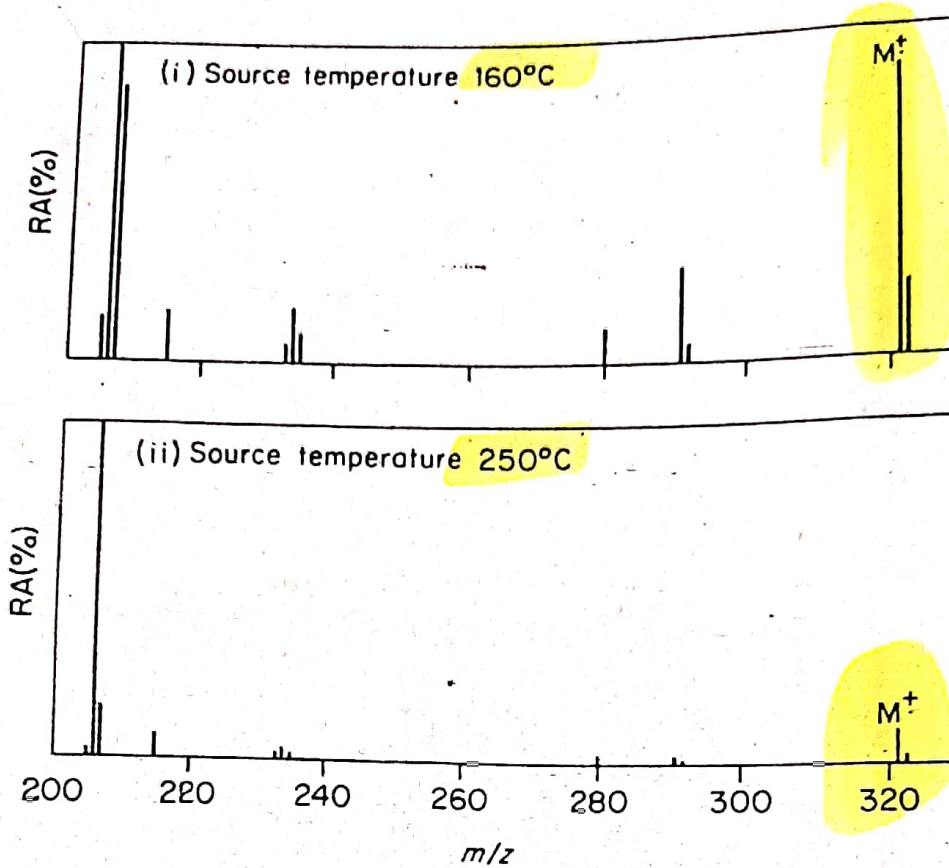


Fig. 3.1g. Mass spectra of the peptide derivative $C_6H_5CH_2OCONHCH(CHMe_2)CONHCH_2COOMe$ recorded at (i) 160 °C and (ii) 250 °C

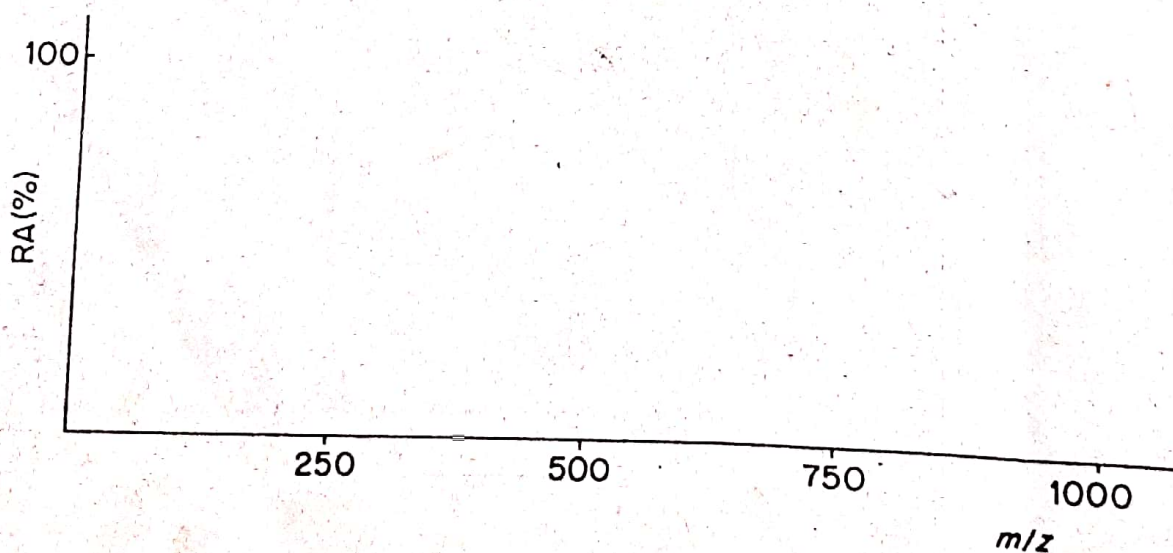


Fig. 3.1h. Mass spectrum of polystyrene

The spectra of the three isomers of $\text{CH}_3\text{C}_6\text{H}_4\text{Cl}$ are all virtually identical and thus it is not possible to distinguish between them.

The mass spectrum of the peptide derivative is markedly dependent on the temperature used for vaporisation. This arises as a consequence of one of two reasons. In some cases thermally unstable molecules dissociate prior to ionisation and thus the observed mass spectrum is that of the decomposition product(s). In other cases relatively high temperatures (250°C or above) are required to obtain volatility and this excess thermal energy, when added to the energy imparted by the ionisation process makes the molecule very prone to fragmentation. This may make it difficult to observe molecular ions and many fragment ions. You may have thought Fig. 3.1h contained a printer's error as no ions are shown. This is not so, the high molecular weight polymer, polystyrene is involatile at temperatures up to 250°C and thus does not give a mass spectrum.

Thus to summarise the drawbacks of electron impact ionisation:

- (i) it may be difficult to measure relative molecular masses for some molecules;
- (ii) it is difficult to distinguish between isomers;
- (iii) some compounds may undergo thermal decomposition prior to ionisation or be very prone to fragmentation after ionisation because of the temperature required for vaporisation;
- (iv) others may simply be too involatile to give a spectrum.

When these problems are encountered, recourse must be made to alternative methods of ionisation. The alternative methods that are in common use when analysis by electron impact is inappropriate are:

- (a) Chemical Ionisation (CI);
- (b) Field Ionisation (FI);
- (c) Field Desorption (FD);
- (d) Fast Atom Bombardment (FAB).

Each of these will now be discussed in some detail.