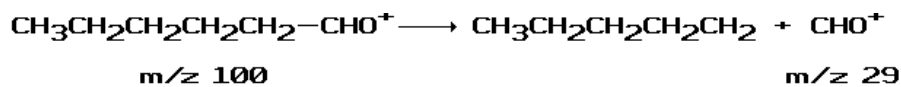# Gas Chromatography - Mass Spectrometry

I.   Introduction

The identification of a complex organic compound by the correlation of its mass spectrum to its structure can be very difficult. The analysis of mixtures can be even more challenging, but can be simplified to a certain extent if the mixture is first separated using a method like gas chromatography. As an introduction to the coupled technique of GC-MS, you will work with a limited number of known, simple compounds and be asked to identify the components of an unknown binary mixture of aldehydes, ketones and/or esters.

In this experiment, the ions needed for the mass spectrum analysis are produced by bombarding the sample with a 70-eV electron beam. A molecular ion (M^+) produced by the loss of a single electron can be produced and will result in a parent peak with the molecular mass of the compound. However, frequently the molecular ion originally produced is left with considerable excess energy. Both the energy and charge are rapidly delocalized, resulting in one or more cleavages with or without some rearrangments. One of the fragments retains the charge and the remaining fragments may be stable molecules or radicals. The kinds of fragments obtained vary with beam energy, however for a 70-eV electron beam most organic molecules fragment in a characteristic and reproducible manner. By noting the differences in the expected fragmentation patterns of aldehydes, ketones and esters (see below) you will identify the presence of specific compounds from these different classes in your unknown.

In simple aliphatic aldehydes the predominant fragmentation involves cleavage alpha to the carbonyl group with loss of the larger alkyl radical. This means that a peak with a mass-to-charge ratio (*m/z*) of 29, corresponding to the formation of CHO^+, is expected. This is illustrated for n-hexanal below.

$$CH_3CH_2CH_2CH_2CH_2{-}CHO^+ \longrightarrow CH_3CH_2CH_2CH_2CH_2 + CHO^+$$

$$\text{m/z } 100 \qquad\qquad\qquad\qquad\qquad \text{m/z } 29$$

If a gamma hydrogen is present, a peak at *m/z* 44 can arise from a process known as the McLafferty rearrangement. This involves gamma hydrogen transfer to the carbonyl oxygen atom with the subsequent formation of $C_2H_5O^+$. This is illustrated below for n-hexanal.
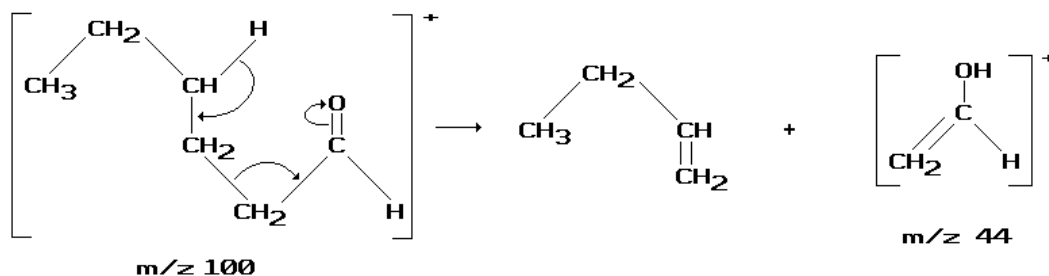
Another peak may result from the McLafferty rearrangement with the charge remaining on the alkyl group (for n-hexanal, a peak at *m/z* 56). Other peaks are possible due to the elimination of small neutral fragments such as CO, CH_3 and H_2O from the parent ion.

Alpha-cleavage is also common for ketones and may occur at either of the two bonds next to the carbonyl group. In general, loss of the larger alkyl fragment is preferred. Thus, for methyl ketones (CH_3-CO-R) a prominent peak at *m/z* 43 (CH_3-CO$^+$) is expected. Gamma-hydrogen transfer may also occur for ketones.

If there is a chain of three or more carbons atoms in each chain of the ketone, then a second McLafferty rearrangement is possible. This is illustrated below for octan-4-one.

m/z 86
(primary enolic product)

m/z 58
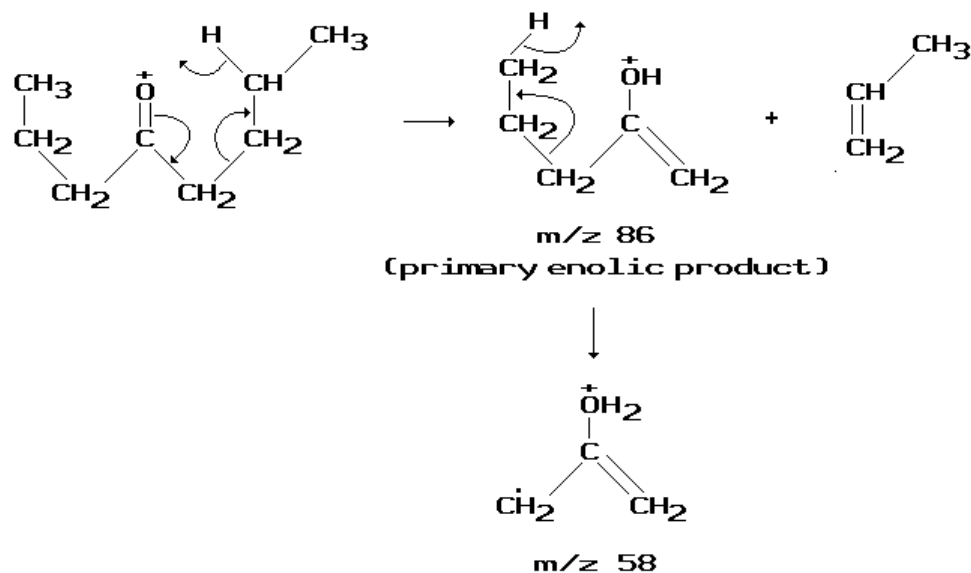
Esters follow a similar fragmentation pattern. They exhibit peaks corresponding to alpha-cleavage on both sides of the carbonyl function, yielding a variety of ions. For example,

$$R_1-\overset{\overset{\displaystyle O}{\|}}{C}-OR_2 \longrightarrow R_1^+, \ R_1-C\equiv O^+, \ [COOR_2]^+, \ ^+OR_2$$
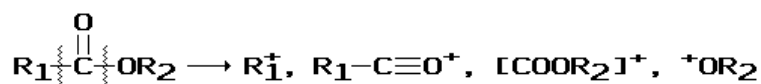
A McLafferty rearrangement is also possible in the presence of gamma hydrogens.

II.   Equipment

   A.   Hewlett Packard Model GCD Mass Spectrometer with 5890 Series II Plus Gas
        Chromatograph and MS ChemStation Computer Interface
   B.   1.0-µL syringe (obtain from the instructor)

III.   Reagents

   A.   Methyl butyrate
   B.   Binary unknown mixture
   C.   Methanol

IV.   Procedure

   A.   Mass Spectrum of Methyl Butyrate

        1.   Use the information given in the Introduction to predict *m/z* values for the principal
             fragments expected for methyl butyrate (butanoic acid methyl ester,
             $CH_3(CH_2)_2COOCH_3$) and tabulate your results.

        2.   When you have completed the analysis of the fragmentation pattern for methyl
             butyrate, your instructor will demonstrate the use of the GC-MS system.

        3.   Ensure that the CHEM422L method has been loaded. Inject about 0.1 µL of
             methyl butyrate into the gas chromatograph and initiate data collection.

        4.   Obtain the integrated mass spectrum for the principal chromatography peak and
             print out the table of *m/z* values. Compare the results with your predicted *m/z*
             values.

   B.   Mass Spectrum of Binary Mixture

        1.   Obtain an unknown from your lab instructor. This unknown is a mixture of two of
             the compounds on the list below.

        2.   Use the procedure in steps IV.A.3 and IV.A.4 to analyze this mixture. However, in
             order for the two components to be separated and eluted efficiently, it may be
             necessary to ramp the column temperature as in the GC experiment. Empirically
             develop a temperature program that will elute both components within 5-6
             minutes. You may want to start the column temperature below 100°C, but in no
             case should you need a temperature higher than 250°C.

V.   Treatment of Data

   A.   Identify the molecular mass of each parent ion by looking for matches between the
        given values and the observed *m/z* values. Once you have identified the two parent
        ion masses, determine the fragmentation pattern expected for each compound on the
        list with that mass and tabulate all results.

B. Determine the identity of the two compounds in your unknown based on a comparison of the expected and observed fragmentation patterns. **Clearly indicate the reasons for your choice of compounds in your unknown and how you eliminated the other possibilities.** In your report, include printouts of the observed mass spectrum and your fragmentation pattern analysis for each compound.

VI. Questions

1. Why doesn't the presence of an expected mass fragment conclusively indicate the presence of a particular compound in your unknown sample?

2. How can the boiling point data for the possible compounds in your unknown assist in the determination of which compounds are present?

Possible Compounds in GC-MS Unknowns

M	Compound	Structure	BP °C
74	ethyl formate	H–C(=O)–OC$_2$H$_5$	54
	methyl acetate	CH$_3$–C(=O)–OCH$_3$	57
	propanoic acid	CH$_3$CH$_2$–C(=O)–OH	141
88	butanoic acid	CH$_3$CH$_2$CH$_2$–C(=O)–OH	165.5
	ethyl acetate	CH$_3$–C(=O)–OC$_2$H$_5$	77.1
	methyl propionate	C$_2$H$_5$–C(=O)–OCH$_3$	79.7
116	tert-butyl acetate	CH$_3$–C(=O)–O–C(CH$_3$)$_3$	98
	methyl valerate	CH$_3$(CH$_2$)$_3$–C(=O)–O–CH$_3$	128
	4-methyl valeric acid	(CH$_3$)$_2$CHCH$_2$CH$_2$–C(=O)–OH	200
176	cinnamyl acetate	HC=CH–CH$_2$–O–C(=O)–CH$_3$ (phenyl)	265
	ethyl cinnamate	HC=CH–C(=O)–O–C$_2$H$_5$ (phenyl)	271
	p-tert-butylacetophenone	CH$_3$–C(=O)–C$_6$H$_4$–C(CH$_3$)$_3$	107-108°/5mm

Lab Cautions for Gas Chromatography - Mass Spectrometry

1. **THE SYRINGES USED FOR INJECTING SAMPLES ARE RATHER FRAGILE. Be especially careful not to bend the plunger. When you are finished running your samples, thoroughly clean the syringe with methanol and return it to the storage drawer.**

2. **Many of the compounds used in this experiment have rather unpleasant odors and sampling should be done in the fume hood.. Do not leave sample vials open to the air except when taking a sample. Do not dispose of these materials except in the appropriate collection containers.**

3. **Recover all sample vials and dispose of them in the GC-MS Vials bucket.**

4. **DO NOT EXIT THE MS PROGRAM WHEN YOU ARE FINISHED. LEAVE THE MONITOR AND COMPUTER ON.**