Chem 325

Mass Spectra
of
Various Classes
of
Organic Compounds

1. Saturated Hydrocarbons

General rules 1-3 apply well to hydrocarbons.
Rearrangements are common but usually do not give intense peaks.
The M⁺ peak of a straight-chain hydrocarbon is always visible, but decreases in intensity as the molecule gets larger. The fragmentation pattern is characterized by peaks separated by 14 mass units (a CH₂ group). The most intense peaks are the C₃ – C₅ fragments.

Branched Hydrocarbons

The MS for branched saturated hydrocarbons are similar, except certain fragments become more prominent.

CI-MS

- For some types of compounds the M⁺ peak is very weak or not observable at all!
- Due to EI ionization being a ‘hard ionization’: so much internal energy is given to the molecular ion that extensive fragmentation immediately results.
- How to measure the molecular mass?!
- Chemical Ionization (CI).
Chemical Ionization

- Ion source filled with relatively high pressure reagent gas, example isobutane i-C₄H₁₀
- Electron impact ionizes the i-C₄H₁₀, high pressure ensures many ion-molecule collisions and reactions to produce C₄H₉⁺, which acts as a protonating agent when it collides with sample molecule M
  
  \[ \text{e} \rightarrow \text{i-C}_4\text{H}_{10} \rightarrow \text{C}_4\text{H}_9^+ \]
  
  \[ \text{C}_4\text{H}_9^+ + \text{M} \rightarrow \text{MH}^+ + \text{C}_4\text{H}_8 \rightarrow (\text{M}+\text{C}_4\text{H}_8)^+ \]

- Can also use \( \text{CH}_4 \), \( \text{NH}_3 \), etc.
  
  ‘soft ionization’: much less fragmentation, can ‘see’ molecular ion

Lambert: all CI mass spectra use i-C₄H₁₀

Cyclic Hydrocarbons

Cyclic hydrocarbons show a much more intense M⁺ ion (Rule 4)

Two bonds must break to form fragments.

2. Alkenes

It is usually easy to see the M⁺ peak of alkenes in EIMS.

In acyclic alkenes, the double bond freely migrates in the fragments, so it can be difficult to determine the double bond location, but for cyclic alkenes it is easier.

Cleavage usually happens at allylic bonds (Rule 5).
3. Aromatic Hydrocarbons

Aromatic hydrocarbons usually show strong M+ peaks (Rule 4). Aromatic rings are stable and have a lower tendency to fragment.

Alkyl substituted benzenes often give a strong peak at m/z 91 due to benzylic cleavage (Rule 8).

4. Alcohols

Alcohols fragment very easily – secondary and primary alcohols show very weak M+ peaks, and tertiary alcohols often do not show M+ at all. MW is often determined by derivatization or CI-MS.

The C-C bond nearest the OH is frequently the first bond to break. Thus primary alcohols often show a prominent peak at 31 m/z.
Alcohols

Sometimes the hydrogen $R_2CH-OH$ in 1° and 2° alcohols cleaves rather than an alkyl group. The result is an M-1 peak.

![Diagram of alcohols cleavage](image1)

Tertiary Alcohols

Tertiary alcohols cleave in a similar fashion to give $CRR-OH$ fragments.

![Diagram of tertiary alcohols cleavage](image2)

More on Alcohols

Alcohols can lose a molecule of water to show a sometimes prominent M-18 peak. It is especially noticeable for primary alcohols.

![Diagram of alcohol cleavage with water loss](image3)

Benzylic Alcohols

Benzylic alcohols fragment much differently from aliphatic alcohols. Benzylic cleavage happens as expected (Rule 8). Benzylic alcohol fragments via the following pathway:

![Diagram of benzylic alcohol cleavage](image4)
Benzylic Alcohols

Benzylic alcohols will usually lose water (M-18). The M-18 peak is especially strong for molecules for which loss of water is mechanistically straightforward.

Phenols

Phenols often show peaks at 77 m/z resulting from formation of phenyl cation, and peaks resulting from loss of CO (M-28) and CHO (M-29) are usually found in phenols.

Example: Octane

If alternative attractive cleavage pathways are available for phenols, the molecule will often take that path.
Example: 4-methyl-2-hexene

Example: 4-methyl-2-pentanol

Example: 3-methyl-1-pentanol

Example: 2-phenylethanol
Example: 1-phenylethanol

Ethers

Cleavage happens in two main ways:
1. Breakage of the C-C bond next to O (like alcohols)

2. C-O bond cleavage with the charge on the C fragment.

5. Ethers

Cleavage happens in two main ways:
1. Breakage of the C-C bond next to O (like alcohols)

Aromatic Ethers

$M^+$ is usually strong. MS is similar to phenols – both form phenoxyl cation (m/z 93) and associated daughters.
6. Ketones

Ketones usually give strong M⁺ peaks. A major fragmentation pathway involves α-cleavage to give an acylium ion.

For ketones with longer chains, the McLafferty rearrangement often leads to strong peaks.

6. Aromatic Ketones

M⁺ is evident. Primary cleavage is α to the carbonyl to give a strong ArCO⁺ peak (m/z 105 when Ar = Ph). This will lose CO to give the phenyl cation (m/z 77).
7. Aldehydes

Aldehydes show weak but discernable M⁺ peaks. Major pathways are α-cleavage and McLafferty Rearrangement.

8. Carboxylic Acids (Aliphatic)

M⁺ is weak, and not always visible. A characteristic m/z 60 peak is often present due to the McLafferty Rearrangement. Bonds α to carbonyl also frequently break to give M-OH and M-CO₂H peaks.

7. Aromatic Aldehydes …

… are similar to aromatic ketones. M⁺ is strong, and M-1 (α-cleavage to carbonyl) is also strong to give the ArCO⁺ ion (m/z 105 for Ar = Ph). Loss of CO from this ion is common to give m/z77 phenyl cation.

Aromatic Acids

M⁺ is very prominent. Common peaks are loss of OH (M-17) and loss of CO₂H (M-45).
**Aromatic Acids**

If an ortho hydrogen-bearing group is present, loss of water (M-18) is visible as well.

\[ \text{OH} \quad \text{O} \quad \text{OH} \quad \text{H} \quad \text{H} \quad \text{O} \quad \text{OH} \quad \text{H} \]

\[ \text{M}^+ = 136 \quad \text{M}^+ = 118 \]

**9. Aliphatic Esters**

\[ \text{M}^+ \text{ is usually distinct. The most characteristic peak is due to the McLafferty rearrangement.} \]

\[ \text{M}^+ = 164 \quad \text{M}^+ = 105 \quad \text{m/z} = 77 \]

**Aromatic Esters**

\[ \text{M}^+ \text{ is usually prominent, unless RO chain is long. The base peak is loss of RO.} \]

\[ \text{M}^+ = 164 \quad \text{H} \quad \text{OH} \quad \text{OH} \quad \text{m/z} = 123 \]

**Aromatic Esters**

The McLafferty rearrangement give the corresponding acid. A more complicated rearrangement often gives a prominent acid+1 peak.
10. Amines

Aliphatic monoamines have odd numbered and weak $M^+$ peaks. Most important cleavage is usually breakage of the C-C bond next to the C-N bond.

Aromatic Amines

$M^+$ is intense (why?). An NH bond can be broken to give a moderately intense M-1 peak.

10. Amines

The base peak in nearly all primary amines comes at 30 m/z.

Aromatic Amines

A common fragmentation is loss of HCN and H$_2$CN to give peaks at 65 and 66 m/z.
### Aromatic Amines

Alkyl substituted aromatic amines typically show breakage of the C-C bond next to the C-N to give a strong peak at 106 when Ar = Ph.

![Aromatic Amines Diagram]

### Amides

Primary amides give a strong peak at m/z 44 due to breakage of the $\text{R-CONH}_2$ bond.

![Amides Diagram]

### 11. Amides

Aliphatic amides – $M^+$ is weak but discernible. For straight-chain amides more than 3 carbons, McLafferty gives the base peak at m/z 59.

![Amides Diagram]

### Aromatic Amides

Any familiar features?
Aromatic Amides

Loss of NH$_2$ to make PhCO$^+$ (105) followed by loss of CO to make the phenyl cation (77). M$^+$ is strong.

Nitriles

Base peak is usually 41 due to a rearrangement like the McLafferty. This has limited diagnostic value since (C$_3$H$_4^+$) has the same mass.

12. Nitriles

M$^+$ are weak or absent for aliphatic nitriles. Loss of the α-hydrogen can give a weak M-1 peak.

13. Nitro compounds

Aliphatic nitro compounds have weak odd M$^+$. The main peaks are hydrocarbon fragments up to M-NO$_2$. 
Aromatic Nitro Compounds

M⁺ is strong. Prominent peaks result from loss of NO₂ radical to give an M-46 peak. Also prominent is M-30 from loss of NO₂.

\[ \text{m/z} = 123 \]
\[ \text{M-46 m/z} = 77 \]
\[ \text{M-30 m/z} = 93 \]