Objectives

After completing this section, you should be able to

1. suggest possible molecular formulas for a compound, given the \( m/z \) value for the molecular ion, or a mass spectrum from which this value can be obtained.
2. predict the relative heights of the \( M^+ \), \((M + 1)^+ \), etc., peaks in the mass spectrum of a compound, given the natural abundance of the isotopes of carbon and the other elements present in the compound.
3. interpret the fragmentation pattern of the mass spectrum of a relatively simple, known compound (e.g., hexane).
4. use the fragmentation pattern in a given mass spectrum to assist in the identification of a relatively simple, unknown compound (e.g., an unknown alkane).

Study Notes

When interpreting fragmentation patterns, you may find it helpful to know that, as you might expect, the weakest carbon-carbon bonds are the ones most likely to break. You might wish to refer to the table of bond dissociation energies when attempting problems involving the interpretation of mass spectra.

This page looks at how fragmentation patterns are formed when organic molecules are fed into a mass spectrometer, and how you can get information from the mass spectrum.

The Origin of Fragmentation Patterns

When the vaporized organic sample passes into the ionization chamber of a mass spectrometer, it is bombarded by a stream of electrons. These electrons have a high enough energy to knock an electron off an organic molecule to form a positive ion. This ion is called the **molecular ion** - or sometimes the **parent ion** and is often given the symbol \( M^+ \) or \( M^+ \cdot \). The dot in this second version represents the fact that somewhere in the ion there will be a single unpaired electron. That's one half of what was originally a pair of electrons - the other half is the electron which was removed in the ionization process.

The molecular ions are energetically unstable, and some of them will break up into smaller pieces. The simplest case is that a molecular ion breaks into two parts - one of which is another positive ion, and the other is an uncharged free radical.

\[
\text{M}^+ \quad \rightarrow \quad X^+ \quad + \quad Y^+
\]

The uncharged free radical will **not** produce a line on the mass spectrum. Only charged particles will be accelerated, deflected and detected by the mass spectrometer. These uncharged particles will simply get lost in the machine - eventually, they get removed by the vacuum pump.

The ion, \( X^+ \), will travel through the mass spectrometer just like any other positive ion - and will produce a line on the stick diagram. All sorts of fragmentations of the original molecular ion are possible - and that means that you will get a
whole host of lines in the mass spectrum. For example, the mass spectrum of pentane looks like this:

![Mass Spectrum of Pentane]

The pattern of lines in the mass spectrum of an organic compound tells you something quite different from the pattern of lines in the mass spectrum of an element. With an element, each line represents a different isotope of that element. With a compound, each line represents a different fragment produced when the molecular ion breaks up.

In the stick diagram showing the mass spectrum of pentane, the line produced by the heaviest ion passing through the machine (at m/z = 72) is due to the molecular ion. The tallest line in the stick diagram (in this case at m/z = 43) is called the base peak. This is usually given an arbitrary height of 100, and the height of everything else is measured relative to this. The base peak is the tallest peak because it represents the commonest fragment ion to be formed - either because there are several ways in which it could be produced during fragmentation of the parent ion, or because it is a particularly stable ion.

### Using Fragmentation Patterns

This section will ignore the information you can get from the molecular ion (or ions). That is covered in three other pages which you can get at via the mass spectrometry menu. You will find a link at the bottom of the page.

**Example 12.2.1: Pentane**

Let's have another look at the mass spectrum for pentane:
What causes the line at m/z = 57?

How many carbon atoms are there in this ion? There cannot be 5 because 5 x 12 = 60. What about 4? 4 x 12 = 48. That leaves 9 to make up a total of 57. How about C$_4$H$_9^+$ then?

C$_4$H$_9^+$ would be [CH$_3$CH$_2$CH$_2$CH$_2$]$,^+$, and this would be produced by the following fragmentation:

$$[\text{C}_3\text{H}_7\text{H}_2\text{H}_2\text{H}_3]^+ \rightarrow [\text{C}_3\text{H}_7\text{H}_2\text{H}_2\text{H}_2]^+ + \cdot \text{CH}_3$$

The methyl radical produced will simply get lost in the machine.

The line at m/z = 43 can be worked out similarly. If you play around with the numbers, you will find that this corresponds to a break producing a 3-carbon ion:

$$[\text{C}_3\text{H}_7\text{H}_2\text{H}_2\text{H}_2]^+ \rightarrow [\text{C}_3\text{H}_7\text{H}_2\text{H}_2]^+ + \cdot \text{CH}_3$$

The line at m/z = 29 is typical of an ethyl ion, [CH$_3$CH$_2$]$^+$:

$$[\text{C}_3\text{H}_7\text{H}_2\text{H}_2\text{H}_2]^+ \rightarrow [\text{C}_3\text{H}_7\text{H}_2]^+ + \cdot \text{CH}_2\text{H}_3$$

The other lines in the mass spectrum are more difficult to explain. For example, lines with m/z values 1 or 2 less than one of the easy lines are often due to loss of one or more hydrogen atoms during the fragmentation process.

Example 12.2.2: Pentan-3-one

This time the base peak (the tallest peak - and so the commonest fragment ion) is at m/z = 57. But this is not produced by the same ion as the same m/z value peak in pentane.
If you remember, the m/z = 57 peak in pentane was produced by \([\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3]^+\). If you look at the structure of pentan-3-one, it's impossible to get that particular fragment from it.

Work along the molecule mentally chopping bits off until you come up with something that adds up to 57. With a small amount of patience, you'll eventually find \([\text{CH}_3\text{CH}_2\text{CO}]^+\) - which is produced by this fragmentation:

\[
[\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3]^+ \rightarrow [\text{CH}_3\text{CH}_2\text{CO}]^+ + \text{CH}_2\text{CH}_3
\]

You would get exactly the same products whichever side of the CO group you split the molecular ion. The m/z = 29 peak is produced by the ethyl ion - which once again could be formed by splitting the molecular ion either side of the CO group.

\[
[\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3]^+ \rightarrow [\text{CH}_3\text{CH}_2\text{CO}]^+ + \text{COCH}_2\text{CH}_3
\]

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**Peak Heights and Stability**

The more stable an ion is, the more likely it is to form. The more of a particular sort of ion that's formed, the higher its peak height will be. We'll look at two common examples of this.

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**Carbocations (carbonium ions)**

Summarizing the most important conclusion from the page on carbocations:

**Order of stability of carbocations**

primary < secondary < tertiary

Applying the logic of this to fragmentation patterns, it means that a split which produces a secondary carbocation is going to be more successful than one producing a primary one. A split producing a tertiary carbocation will be more successful still. Let's look at the mass spectrum of 2-methylbutane. 2-methylbutane is an isomer of pentane - isomers are molecules with the same molecular formula, but a different spatial arrangement of the atoms.
Look first at the very strong peak at m/z = 43. This is caused by a different ion than the corresponding peak in the pentane mass spectrum. This peak in 2-methylbutane is caused by:

\[
\begin{align*}
\left[ \text{CH}_3\text{O}+\text{CH}_2\text{CH}_3 \right]^+ & \quad \rightarrow \quad \text{CH}_3\text{CH}^+ + \text{CH}_2\text{CH}_3 \\
\end{align*}
\]

The ion formed is a secondary carbocation - it has two alkyl groups attached to the carbon with the positive charge. As such, it is relatively stable. The peak at m/z = 57 is much taller than the corresponding line in pentane. Again a secondary carbocation is formed - this time, by:

\[
\begin{align*}
\left[ \text{CH}_3\text{O}+\text{CH}_2\text{CH}_3 \right]^+ & \quad \rightarrow \quad \text{CH}_3\text{CH}^+ + \text{CH}_2\text{CH}_3 \\
\end{align*}
\]

You would get the same ion, of course, if the left-hand CH\textsubscript{3} group broke off instead of the bottom one as we've drawn it. In these two spectra, this is probably the most dramatic example of the extra stability of a secondary carbocation.

**Acylium ions, [RCO]^+**

Ions with the positive charge on the carbon of a carbonyl group, C=O, are also relatively stable. This is fairly clearly seen in the mass spectra of ketones like pentan-3-one.
The base peak, at m/z=57, is due to the \([\text{CH}_3\text{C}_2\text{O}]^+\) ion. We've already discussed the fragmentation that produces this.

**Note**

The more stable an ion is, the more likely it is to form. The more of a particular ion that is formed, the higher will be its peak height.

**Using mass spectra to distinguish between compounds**

Suppose you had to suggest a way of distinguishing between pentan-2-one and pentan-3-one using their mass spectra.

- **pentan-2-one** \(\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3\)
- **pentan-3-one** \(\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3\)

Each of these is likely to split to produce ions with a positive charge on the \(\text{CO}\) group. In the pentan-2-one case, there are two different ions like this:

- \([\text{CH}_3\text{C}_2\text{O}]^+\)
- \([\text{COCH}_2\text{CH}_2\text{CH}_3]^+\)

That would give you strong lines at m/z = 43 and 71. With pentan-3-one, you would only get one ion of this kind:

- \([\text{CH}_3\text{CH}_2\text{CO}]^+\)

In that case, you would get a strong line at 57. You don't need to worry about the other lines in the spectra - the 43, 57 and 71 lines give you plenty of difference between the two. The 43 and 71 lines are missing from the pentan-3-one spectrum, and the 57 line is missing from the pentan-2-one one.

The two mass spectra look like this:
As you've seen, the mass spectrum of even very similar organic compounds will be quite different because of the different fragmentation patterns that can occur. Provided you have a computer data base of mass spectra, any unknown spectrum can be computer analyzed and simply matched against the data base.

Exercises

Questions

Q12.2.1

Caffeine has a mass of 194.19 amu, determined by mass spectrometry, and contains C, N, H, O. What is a molecular formula for this molecule?

Q12.2.2

The following are the spectra for 2-methyl-2-hexene and 2-heptene, which spectra belongs to the correct molecule. Explain.

A:
SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, 2 December 2016)

**Solutions**

**S12.2.1**

C₈H₁₀N₄O₂

C = 12 × 8 = 96

N = 14 × 4 = 56

H = 1 × 10 = 10

O = 2 × 16 = 32

96+56+10+32 = 194 g/mol
The (A) spectrum is 2-methyl-2-hexene and the (B) spectrum is 2-heptene. Looking at (A) the peak at 68 \textit{m/z} is the fractioned molecule with just the tri-substituted alkene present. While (B) has a strong peak around the 56 \textit{m/z}, which in this case is the di-substituted alkene left behind from the linear heptene.

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**Objective**

After completing this section, you should be able to predict the expected fragmentation for common functional groups, such as alcohols, amines, and carbonyl compounds.

**Key Terms**

Make certain that you can define, and use in context, the key terms below.

- alpha (\(\alpha\)) cleavage
- McLafferty rearrangement

Much of the utility in electron-ionization MS comes from the fact that the radical cations generated in the electron-bombardment process tend to fragment in predictable ways. Detailed analysis of the typical fragmentation patterns of different functional groups is beyond the scope of this text, but it is worthwhile to see a few representative examples, even if we don’t attempt to understand the exact process by which the fragmentation occurs. We saw, for example, that the base peak in the mass spectrum of acetone is \textit{m/z} = 43. This is the result of cleavage at the ‘alpha’ position - in other words, at the carbon-carbon bond adjacent to the carbonyl. Alpha cleavage results in the formation of an acylium ion (which accounts for the base peak at \textit{m/z} = 43) and a methyl radical, which is neutral and therefore not detected.

\[
\text{H}_3\text{C}\text{C} \equiv \text{O}^+ + \cdot\text{CH}_3
\]

After the parent peak and the base peak, the next largest peak, at a relative abundance of 23%, is at \textit{m/z} = 15. This, as
you might expect, is the result of formation of a methyl cation, in addition to an acyl radical (which is neutral and not detected).

\[ \text{molecular ion} \rightarrow \text{acyl radical} + \text{methyl cation} \]

A common fragmentation pattern for larger carbonyl compounds is called the **McLafferty rearrangement**:

The mass spectrum of 2-hexanone shows a 'McLafferty fragment' at m/z = 58, while the propene fragment is not observed because it is a neutral species (remember, only cationic fragments are observed in MS). The base peak in this spectrum is again an acylium ion.

When alcohols are subjected to electron ionization MS, the molecular ion is highly unstable and thus a parent peak is often not detected. Often the base peak is from an ‘oxonium’ ion.
Other functional groups have predictable fragmentation patterns as well. By carefully analyzing the fragmentation information that a mass spectrum provides, a knowledgeable spectrometrist can often ‘put the puzzle together’ and make some very confident predictions about the structure of the starting sample.

Click here for examples of compounds listed by functional group, which demonstrate patterns which can be seen in mass spectra of compounds ionized by electron impact ionization.

Example 12.3.1

The mass spectrum of an aldehyde gives prominent peaks at $m/z = 59$ (12%, highest value of $m/z$ in the spectrum), 58 (85%), and 29 (100%), as well as others. Propose a structure, and identify the three species whose $m/z$ values were listed.

Solution

Exercises

Questions

Q12.3.1
What are the masses of all the components in the following fragmentations?

Solutions

S12.3.1

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