Chemistry 5652

Spectroscopic Identification of Organic Compounds

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Room BH222

Text: *Introduction to Spectroscopy, Pavia, Lampman, Kriz*
Go to the web at: www.umsl.edu/~chickosj/
Open Chem 5652
What is the first thing we need to know to determining molecular structure?

Elemental Composition

Determination of Empirical Formula

a. How is empirical formula determined

Combustion Analysis

Example: Suppose 15.2 mg sample of an unknown compound was burned in an excess of oxygen to produce 43.0 mg CO₂ and 15.6 mg H₂O. What is a possible empirical formula?
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mass of H in H₂O \( \frac{2}{18} = 0.1111 \); mass of C in CO₂ \( \frac{12}{44} = 0.2727 \)

\[
0.1111 \times 15.6 = 1.73 \text{ mg H;}
\]
\[
0.2727 \times 43.0 = 11.7 \text{ mg C}
\]
\[
13.43 \text{ mg}
\]

\[15.2 - 13.43 = 1.77 \text{ mg O, S, N?}\]

Simplest ratio

H: \[ \frac{1.73 \text{ mg}}{1 \text{ mg/mmol}} = 1.73 \text{ mmol} \]
C: \[ \frac{11.7 \text{ mg}}{12 \text{ mg/mmol}} = 0.975 \text{ mmol} \]
O: \[ \frac{1.77 \text{ mg}}{16 \text{ mg/mmol}} = 0.111 \text{ mmol} \]

Which mmol value is best known?

C: \( \frac{0.975}{0.975} = 1.0 \)
H: \( \frac{1.74}{0.975} = 1.78 \)
O: \( \frac{0.111}{0.975} = 0.114 \)
Empirical formula: $\text{C}_9\text{H}_{16}\text{O}$ or $\text{C}_{18}\text{H}_{32}\text{S}$

Possible molecular formulas: $\text{C}_{9n}\text{H}_{16n}\text{O}_n$ or $\text{C}_{18n}\text{H}_{32n}\text{S}$

where $n = 1, 2, 3, \ldots$
Determination of Molecular Formula

a. Nominal mass determination (combustion analysis coupled with: pH titration, freezing point depression, mass spectrometry)

b. Exact mass measurement
Measurement of molecular formula and molecular weight is frequently accomplished by measuring the exact mass by mass spectrometry.
The nominal mass of a substance is 140. What is its molecular formula? The rule of 13:

1. Divide the nominal mass by 13: $140/13 = 10.769$; A hydrocarbon with this molecular weight would have 10 C atoms
2. Multiply the remainder by 13: $0.769 \times 13 = 9.997$ or 10; A hydrocarbon with this molecular weight would have $(10+10)$ or 20 H
3. For every O subtract 16 ($1C + 4 H$ or $16 H$) = $C_{9}H_{16}O$; $C_{8}H_{12}O_{2}$
4. $C_{7}H_{8}O_{3}$; $C_{6}H_{4}O_{4}$
Summary

Rule of 13
number of C = MW/13  (the digits before the decimal point)
number of H = (the number of C atoms plus 13*digits after the decimal)

Once determining the number of carbons and hydrogens, subtract
for each oxygen:  16 (1C+4H; 16 H)
for each sulfur  : 32 (2C+8H; 32 H)
for each nitrogen: 14 (C+2H, 14 H)
...
Exact Mass Measurements
<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Weight</th>
<th>Isotope</th>
<th>Exact Mass</th>
</tr>
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<td>$^1$H</td>
<td>1.0080</td>
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<tr>
<td></td>
<td></td>
<td>$^2$D</td>
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<tr>
<td>Iodine</td>
<td>126.9045</td>
<td>$^{127}$I</td>
<td>126.9045</td>
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</tbody>
</table>
Why is the atomic weight of C not exactly 12.000?

Carbon consists of two isotopes, $^{12}\text{C}$ (99 %) and $^{13}\text{C}$ (1%).

Remember atomic weight is defined as an weighted average of all isotopes.
Exact Mass Measurements

What is exact mass? $m$

mass of a proton: $1.672623 \times 10^{-24}$ g

mass of a neutron: $1.674927 \times 10^{-24}$ g

mass of a deuteron: $3.3427 \times 10^{-24}$ g

Avogadro’s Number (AN): $6.0254 \times 10^{23}$

Molar mass of $^2$D = AN* $m_D = 6.0254 \times 10^{23} \times 3.3427 \times 10^{-24}$ g

$= 2.0141$ g mol$^{-1}$

Carbon = 6 $^2$D = 6*2.0141 = 12.0846;

Carbon = 6(P +N) = 6(1.672623+1.674927)*0.60254 =12.1022

Exact mass of carbon = 12.0 Why the discrepancies?
E = Δm C^2

Where E is the energy given off from a mass discrepancy of m and C is the speed of light.

E = 0.0846 g · (3*10^{10} \text{ cm sec}^{-1})^2

E = g · \text{cm} · (\text{sec}^{-1})^2 · \text{cm}

E = \text{force} · \text{distance}
stability. In Figure 2 this quantity B.E./A is plotted as a function of A. The maxima at certain values (e.g., 4, 12, etc.) reflect unusual stability for these values of A. Calculations of this type may be used to demonstrate that above bismuth, emission of alpha particles is exoergic. This accounts for alpha activity in the heavy elements.

Figure 2. Plot of the binding energy per nucleon (Mev/nucleon) as a function of the mass number.
Using Exact Mass Measurements

Suppose you determined the exact mass of an ion by mass spectrometry to be 56.0376. Nominal mass 56
How can you figure out all the possible formulas that add to 56?

First use the Rule of 13

Divide the nominal mass by thirteen; the number in front of the decimal is the number of carbons; multiply the number following the decimal by 13 and add it to the number of carbons; this equals the number of hydrogens.

a. To add an oxygen: remove a carbon and 4 hydrogens
b. To add a nitrogen: remove a carbon and 2 hydrogens
c. To add a sulfur: remove two carbons, 6 hydrogens; or 2 oxygens
d. …
Mass of 56  
56/13 = 4.3076;  The number of carbons is 4  
13*0.3076 = 4; therefore the number of hydrogens is 4 + 4  
Therefore the hydrocarbon formula is C₄H₈  
Other possible molecular formulas are:

C₄H₈ - CH₄ = C₃H₄O  
C₄H₈ - CH₂ = C₃H₆N  X  
C₄H₈ - 2CH₄ = C₂O₂ ;  C₄H₈ - 2CH₄ = C₂S ;  
C₄H₈ - 2CH₂ = C₂H₄N₂  
C₄H₈ - CH₄, CH₂ = C₂H₂NO  X  
C₄H₈ - 3CH₂ = CH₂N₃  X  
C₄H₈ - C = C₃H₂₀  X  
C₄H₈ - CH₄, 2CH₂ = CN₂O  C₄H₈ - 4CH₂ = N₄  

All compounds with an odd number of nitrogen atoms must have an odd molecular weight  
X
The exact mass of an ion by mass spectrometry was determined to be 56.0376 amu

<table>
<thead>
<tr>
<th>Nominal mass 56</th>
<th>exact mass</th>
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<tbody>
<tr>
<td>N\textsubscript{4}</td>
<td>4*14.0031</td>
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<tr>
<td>CN\textsubscript{2}O</td>
<td>12.00+2*14.0031+15.9949</td>
</tr>
<tr>
<td>CH\textsubscript{2}N\textsubscript{3}</td>
<td>...</td>
</tr>
<tr>
<td>C\textsubscript{2}O\textsubscript{2}</td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{2}NO</td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{4}N\textsubscript{2}</td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{4}O</td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{6}N</td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{4}H\textsubscript{8}</td>
<td></td>
</tr>
</tbody>
</table>
Determining Molecular Formulas and Degree of Unsaturation

What is the degree of unsaturation of this compound?

\[ \text{C}_{19}\text{H}_{17}\text{ClN}_2\text{O} \] prazepam

Draw a structure of a compound with the same number of carbons and heteroatoms that contains no rings or double bonds; each carbon should have 4 bonds, each O should have 2 bonds each nitrogen should have three bonds …

\[ \text{NH}_2\text{CH}_2\text{CHOHCHClCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{H}_2 \]

\[ \text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{H}_2 \]

Molecular formula is \( \text{C}_{19}\text{H}_{41}\text{ClN}_2\text{O} \)

\[ \text{C}_{19}\text{H}_{41}\text{ClN}_2\text{O} - \text{C}_{19}\text{H}_{17}\text{ClN}_2\text{O} = 24/2 = 12 \text{ degrees of unsaturation} \]
What is the origin of the small peak at m/e of 141
<table>
<thead>
<tr>
<th>Elements</th>
<th>Isotope</th>
<th>Relative Abundance</th>
<th>Isotope</th>
<th>Relative Abundance</th>
<th>Isotope</th>
<th>Relative Abundance</th>
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<tbody>
<tr>
<td>Carbon</td>
<td>$^{12}\text{C}$</td>
<td>100</td>
<td>$^{13}\text{C}$</td>
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<tr>
<td>Oxygen</td>
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<td>Silicon</td>
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<td>Bromine</td>
<td>$^{79}\text{Br}$</td>
<td>100</td>
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<tr>
<td>Iodine</td>
<td>$^{127}\text{I}$</td>
<td>100</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
What is the origin of the peak at 141; called the P+1 peak
For a molecular formula of C$_9$H$_{16}$O, what’s the probability of having 1 $^{13}$C?
Probability is $(X+Y)^n$ where X and Y is the probability of having isotope $^{12}$C and $^{13}$C, respectively and n is the number of C atoms

$(^{12}$C +$^{13}$C)$^9$

\[
\begin{array}{cccccccccc}
1 & & & & & & & & & \\
1 & 1 & & & & & & & & \\
1 & 2 & 1 & & & & & & & \\
1 & 3 & 3 & 1 & & & & & & \\
1 & 4 & 6 & 4 & 1 & & & & & \\
1 & 5 & 10 & 10 & 5 & 1 & & & & \\
1 & 6 & 15 & 20 & 15 & 6 & 1 & & & \\
1 & 7 & 21 & 35 & 35 & & & & & \\
1 & 8 & 28 & 56 & 56 & & & & & \\
1 & 9 & 36 & 84 & & & & & & \\
\end{array}
\]

$(^{12}$C)$^9$ + 9$(^{12}$C)$^8$(^{13}$C) +36$(^{12}$C)$^7$(^{13}$C)^2

All $^{12}$C $^{13}$C $^{13}$C

$(0.989)^9 = 0.905$; \quad 9(0.989)^8(0.011)= 0.091; \quad 36(0.989)^7(0.011)^2 = 0.004

(0.905/0.905)*100 = 100% \quad (0.091/0.905)*100 = 10% \quad (0.004/0.905)*100 = 0.45%
The parent ion is reported as 100%.

Then 
\[(0.989)^9 = 100(0.905/0.905) = 100\%\]
9\[(0.989)^8(0.011) = 100(0.091/0.905) = 10.0\%\]
36\[(0.989)^7(0.011)^2 = 0.004/0.905 = 0.45\%\]

Including 1 oxygen: $^{17}\text{O} = 0.04$
$^{18}\text{O} = 0.2$

P = 100 %
P+1 = 10.04 %
P+2 = 0.65 %
The contribution of $^{2}\text{H}$ is pretty small
Electron impact mass spectrum of $\text{CCl}_4$

152 - 117 = 35
100%/(100+32.5) = 0.7547 $^{35}\text{Cl}$

1.0-0.7547 = 0.2452 $^{37}\text{Cl}$
\((^{35}\text{Cl} + ^{37}\text{Cl})^3\)

\[
\begin{array}{ccc}
1 \\
1 & 1 & 1 \\
1 & 2 & 1 \\
1 & 3 & 3 & 1 \\
1 & 4 & 6 & 4 & 1 \\
\end{array}
\]

\(n = 1\)

\[(0.7547)^3 \quad 3(0.7547)^2(0.2453) \quad 3(0.7547)(0.2453)^2 \quad (0.2453)^3\]

0.43 \quad 0.419 \quad 0.136 \quad 0.0148

100% \quad 97.5% \quad 31.7% \quad 3.4%

For CCl\(_4\)

\[(0.7547)^4 \quad 4(0.7547)^3(0.2453) \quad 6(0.7547)^2(0.2453)^2 \quad 4(0.7547)(0.2453)^3\]

0.324 \quad 0.4226 \quad 0.206 \quad 0.045

100% \quad 130% \quad 63.4% \quad 13.7%

\[(0.2453)^4\]

0.0036

1.1%
What about other elements?
Organic Spectroscopy

Our knowledge of the universe has come about primarily as a result of our studies of how light interacts with matter.

Unlike our macroscopic world in which things seem continuous, events occur at the atomic scale in discrete steps.

Models
A More Extensive View of The Electromagnetic Spectrum