Welcome!!

Chemistry 328N

Organic Chemistry for Chemical Engineers

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Teaching Assistants: Michael Maher and Garret Blake

http://willson.cm.utexas.edu

January 19, 2016
Your Teaching Assistants

Michael Maher  
Garret Blake

Please take advantage of the scheduled office hours

Chemistry 328N
Bureaucracy:

- Please read the syllabus carefully
- Attend all lectures
- Do the homework
- Don’t get behind
- Take advantage of office hours
  - We want to get to know you
- Watch the web page
  - http://willson.cm.utexas.edu (teaching)
- Keep up with the work!
- You can’t “cram” for the exams in this class
- Don’t get behind!!
Mass Spectrometry

**Base Peak**

**Molecular ion**
A Mass Spectrometer

- A mass spectrometer is designed to do three things:

  1. Convert neutral atoms or molecules into a beam of positive (or negative) ions

  2. Separate the ions on the basis of their mass-to-charge ratio (m/z)

  3. Measure the relative abundance of each ion

http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/MassSpec/massspec1.htm
Mass Spectrometer

1. inject sample
2. heater to vapourise sample
3. electron beam ionises sample
4. particles accelerated into magnetic field
5. magnetic field separates particles based on mass/charge ratio

charged particle beam
lightest
heaviest
Detector

X⁺ Y⁺ Z⁺
In here

magnet

Out here

Scientist
Modern Mass Spectrometer
unit mass resolution

Mass Spectrometer

Scientist
A Mass Spectrometer

- Electron ionization MS
  - In the ionization chamber, the sample is bombarded with a beam of high-energy electrons
  - Collisions between these electrons and the sample result in loss of electrons from sample molecules and formation of positive ions

\[
\text{H} - \text{C} - \text{H} + e^- \rightarrow \left[ \begin{array}{c} \text{H} \\ \text{H} \end{array} \right]^+ + 2e^-
\]

Molecular ion (A radical cation)
Molecular Ion

- **Molecular ion** (M or M⁺): the species formed by removal of a single electron from a molecule.

- For our purposes, it does not matter which electron is lost; radical cation character is delocalized throughout the molecule. Therefore, we write the molecular formula of the parent molecule in brackets with:
  - A plus sign to show that it is a cation
  - A dot to show that it has an odd number of electrons

\[
[\text{CH}_3\text{CH}_2\text{OCH}_3]^+ 
\]
At times, however, we find it useful to depict the radical cation at a certain position in order to better understand its reactions:

\[
\text{[CH}_3\text{CH}_2\text{OCH(CH}_3\text{)}_2\text{]}^+ \quad \text{[CH}_3\text{CH}_2\text{OCH(CH}_3\text{)}_2\text{]}^+
\]
Mass Spectrum

- **Mass spectrum**: a plot of the relative abundance of each ion versus mass-to-charge ratio

- **Base peak**: the most abundant peak; assigned an arbitrary intensity of 100

- The relative abundance of all other ions is reported as a % of abundance of the base peak
Mass Spectrum of 1-Butene

![Graph showing the mass spectrum of 1-butene with labeled peaks and molecular ion.]
The Nitrogen Rule

- Nitrogen rule: if a compound has
  - zero or an even number of nitrogen atoms, its molecular ion will have an *even* m/z value
  - an odd number of nitrogen atoms, the molecular ion will have an *odd* m/z value
Other MS Techniques

- What we have described is called electron ionization mass spectrometry (EI MS)

- Other techniques include
  - Fast atom bombardment (FAB)
  - Matrix assisted laser desorption ionization (MALDI)
  - Chemical ionization (CI)
  - And many others….
Resolution

- **Resolution**: a measure of how well a mass spectrometer separates ions of different mass.

  - **Low resolution** - capable of distinguishing among ions of different nominal mass, that is ions that differ by at least one or more atomic mass units (Daltons).

  - **High resolution** - capable of distinguishing among ions that differ in mass by as little as 0.0001 mass units.
High Resolution Mass Spectrometer
Resolution

- C\textsubscript{3}H\textsubscript{6}O and C\textsubscript{3}H\textsubscript{8}O have nominal masses of 58 and 60 respectively, and can be readily distinguished by low-resolution MS.

- C\textsubscript{2}H\textsubscript{4}O\textsubscript{2} and C\textsubscript{3}H\textsubscript{8}O both have a nominal mass of 60. However, we can still distinguish between them by high-resolution MS.

<table>
<thead>
<tr>
<th>Molecular Formula</th>
<th>Nominal Mass</th>
<th>Precise Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{3}H\textsubscript{8}O</td>
<td>60</td>
<td>60.05754</td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{4}O\textsubscript{2}</td>
<td>60</td>
<td>60.02112</td>
</tr>
</tbody>
</table>

Chemistry 328N
Differences are due to Isotopes

- In nature Carbon is 98.90% $^{12}\text{C}$ and 1.10% $^{13}\text{C}$. Thus, there are 1.11 atoms of carbon-13 in nature for every 100 atoms of carbon-12...Mass spectroscopists use this measure rather than %!!!!!!

$$\left[\frac{1.10 \ ^{13}\text{C}}{98.90 \ ^{12}\text{C}}\right] \times 100 \ ^{12}\text{C} \ \text{atoms} = 1.11 \ ^{13}\text{C} \ \text{per} \ 100 \ ^{12}\text{C}$$

- The “relative abundance” of $^{13}\text{C}$ is defined as 1.11
## Precise masses and natural abundances of isotopes

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Weight</th>
<th>Isotope</th>
<th>Precise Mass (amu)</th>
<th>Relative Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrogen</td>
<td>1.0079</td>
<td>${^1\text{H}}$</td>
<td>1.00783</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>${^2\text{H}}$</td>
<td>2.01410</td>
<td>0.016</td>
</tr>
<tr>
<td>carbon</td>
<td>12.011</td>
<td>${^{12}\text{C}}$</td>
<td>12.0000</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>${^{13}\text{C}}$</td>
<td>13.0034</td>
<td>1.11</td>
</tr>
<tr>
<td>nitrogen</td>
<td>14.007</td>
<td>${^{14}\text{N}}$</td>
<td>14.0031</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>${^{15}\text{N}}$</td>
<td>15.0001</td>
<td>0.38</td>
</tr>
<tr>
<td>oxygen</td>
<td>15.999</td>
<td>${^{16}\text{O}}$</td>
<td>15.9949</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>${^{17}\text{O}}$</td>
<td>16.9991</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>${^{18}\text{O}}$</td>
<td>17.9992</td>
<td>0.20</td>
</tr>
<tr>
<td>sulfur</td>
<td>32.066</td>
<td>${^{32}\text{S}}$</td>
<td>31.9721</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>${^{33}\text{S}}$</td>
<td>32.9715</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td></td>
<td>${^{34}\text{S}}$</td>
<td>33.9679</td>
<td>4.40</td>
</tr>
<tr>
<td>chlorine</td>
<td>35.453</td>
<td>${^{35}\text{Cl}}$</td>
<td>34.9689</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>${^{37}\text{Cl}}$</td>
<td>36.9659</td>
<td>32.5</td>
</tr>
<tr>
<td>bromine</td>
<td>79.904</td>
<td>${^{79}\text{Br}}$</td>
<td>78.9183</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>${^{81}\text{Br}}$</td>
<td>80.9163</td>
<td>98.0</td>
</tr>
</tbody>
</table>
# Calculation of Precise Mass

Use mass of most abundant isotope...why??

\[ \text{C}_3\text{H}_8\text{O} \text{ and } \text{C}_2\text{H}_4\text{O}_2 \]

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>( \text{C} )</th>
<th>( \text{H} )</th>
<th>( \text{O} )</th>
<th>SUM</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>12</td>
<td>3</td>
<td>36</td>
<td>2</td>
<td>24</td>
</tr>
<tr>
<td>H</td>
<td>1.00783</td>
<td>8</td>
<td>8.06264</td>
<td>4</td>
<td>4.03132</td>
</tr>
<tr>
<td>O</td>
<td>15.9949</td>
<td>1</td>
<td>15.9949</td>
<td>2</td>
<td>31.9898</td>
</tr>
<tr>
<td>SUM</td>
<td></td>
<td></td>
<td>60.05754</td>
<td>60.02112</td>
<td></td>
</tr>
</tbody>
</table>

http://www.colby.edu/chemistry/NMR/IsoClus.html
Calculating M+1

- $M + 1 = \sum [(\text{abundance of heavier isotope}) \times (\text{number of atoms in the empirical formula})]$
- Thus, for octane, $C_8H_{18}$

$$M + 1 = \sum ((1.11 \times 8) + (0.016 \times 18))$$
$$= 8.88 + 0.288$$
$$= 9.17\% \text{ of } M$$
Calculated Spectrum

Formula: C₈H₁₈

<table>
<thead>
<tr>
<th>mass</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>114</td>
<td>100.0</td>
</tr>
<tr>
<td>115</td>
<td>8.8</td>
</tr>
<tr>
<td>116</td>
<td>0.3</td>
</tr>
<tr>
<td>117</td>
<td>0.0</td>
</tr>
</tbody>
</table>

M+1 peak

http://www.sisweb.com/mstools/isotope.htm
http://www.chemcalc.org/
http://fluorine.ch.man.ac.uk/research/mstool2.php
Calculated Spectrum

Formula: $C_2H_5Br_1$

<table>
<thead>
<tr>
<th>Mass</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>108</td>
<td>100.0</td>
</tr>
<tr>
<td>109</td>
<td>2.2</td>
</tr>
<tr>
<td>110</td>
<td>97.3</td>
</tr>
<tr>
<td>111</td>
<td>2.2</td>
</tr>
<tr>
<td>112</td>
<td>0.0</td>
</tr>
</tbody>
</table>

An M+2 peak!!

http://www.sisweb.com/mstools/isotope.htm

## Isotopes

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass Number</th>
<th>Mass</th>
<th>Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxygen</td>
<td>15.999</td>
<td>16(^{16})O</td>
<td>15.9949</td>
</tr>
<tr>
<td></td>
<td></td>
<td>17(^{17})O</td>
<td>16.9991</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18(^{18})O</td>
<td>17.9992</td>
</tr>
<tr>
<td>sulfur</td>
<td>32.066</td>
<td>32(^{32})S</td>
<td>31.9721</td>
</tr>
<tr>
<td></td>
<td></td>
<td>33(^{33})S</td>
<td>32.9715</td>
</tr>
<tr>
<td></td>
<td></td>
<td>34(^{34})S</td>
<td>33.9679</td>
</tr>
<tr>
<td>chlorine</td>
<td>35.453</td>
<td>35(^{35})Cl</td>
<td>34.9689</td>
</tr>
<tr>
<td></td>
<td></td>
<td>37(^{37})Cl</td>
<td>36.9659</td>
</tr>
<tr>
<td>bromine</td>
<td>79.904</td>
<td>79(^{79})Br</td>
<td>78.9183</td>
</tr>
<tr>
<td></td>
<td></td>
<td>81(^{81})Br</td>
<td>80.9163</td>
</tr>
</tbody>
</table>
M+2 Peaks

- Sulfur is the only other element common to organic compounds that gives a significant M + 2 peak and it is small

\[ ^{32}S = 95.02\% \text{ and } ^{34}S = 4.21\% \]

Result of isotope pattern calculation
Formula: C1H4S1
mass %
48 100.0 __________________~______________________________
49 1.9 _
50 4.5 _
Possible ways of combining two Chlorines
- 35-35 (70), 35-37 (72) and 37-37 (74)
- Three peaks of what relative intensity?
- Assume that the probability of 35 is 0.75 and of 37 is 0.25 (close to true)

<table>
<thead>
<tr>
<th>First Cl</th>
<th>35</th>
<th>35</th>
<th>35</th>
<th>35</th>
</tr>
</thead>
<tbody>
<tr>
<td>second Cl</td>
<td>35</td>
<td>35</td>
<td>35</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>35</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>total</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>74</td>
</tr>
</tbody>
</table>

From the table

<table>
<thead>
<tr>
<th>Mass 70 = 9</th>
<th>Relative Probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>9/16 = 0.5625</td>
<td>/ 0.5625 = 1.00</td>
</tr>
<tr>
<td>Mass 72 = 6</td>
<td>6/16 = 0.375</td>
</tr>
<tr>
<td></td>
<td>/ 0.5625 = .666</td>
</tr>
<tr>
<td>Mass 74 = 1</td>
<td>1/16 = 0.0625</td>
</tr>
<tr>
<td></td>
<td>/ 0.5625 = .111</td>
</tr>
<tr>
<td>Total = 16</td>
<td></td>
</tr>
</tbody>
</table>

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Another way.... To look at this

<table>
<thead>
<tr>
<th>Permutations</th>
<th>Probability Product</th>
<th>Frequency</th>
<th>Probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>35,35</td>
<td>0.75 x 0.75</td>
<td>1</td>
<td>0.5625</td>
</tr>
<tr>
<td>35,37 (or 37,35)</td>
<td>0.75 x 0.25</td>
<td>2</td>
<td>0.3750</td>
</tr>
<tr>
<td>37,37</td>
<td>0.25 x 0.25</td>
<td>1</td>
<td>0.0625</td>
</tr>
</tbody>
</table>

(0.5625 / 0.5625) x 100 = **100**

(0.3750 / 0.5625) x 100 = **66.6**

(0.0625 / 0.5625) x 100 = **11.1**
What is Wrong with these things??

- Using more *exact isotope masses*

<table>
<thead>
<tr>
<th></th>
<th>Mass Formula</th>
<th>Count</th>
<th>Percentage</th>
<th>Calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>35,35</td>
<td>$0.7577 \times 0.7577$</td>
<td>1</td>
<td>0.5741</td>
<td>$\frac{0.5741}{0.5741} \times 100 = 63.9$</td>
</tr>
<tr>
<td>35,37 (or 37,35)</td>
<td>$0.7577 \times 0.2423$</td>
<td>2</td>
<td>0.3671</td>
<td>$(0.3671/0.5741) \times 100 = 63.9$</td>
</tr>
<tr>
<td>37,37</td>
<td>$0.2423 \times 0.2423$</td>
<td>1</td>
<td>0.05871</td>
<td>$\frac{0.05871}{0.5741} \times 100 = 10.2$</td>
</tr>
<tr>
<td>Element</td>
<td>Symbol</td>
<td>Nominal Mass</td>
<td>Exact Mass</td>
<td>Abundance</td>
</tr>
<tr>
<td>---------</td>
<td>--------</td>
<td>--------------</td>
<td>------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H(\text{D or } ^2\text{H})</td>
<td>1 2</td>
<td>1.00783 2.01410</td>
<td>99.99 0.01</td>
</tr>
<tr>
<td>Carbon</td>
<td>(^{12}\text{C}) (^{13}\text{C})</td>
<td>12 13</td>
<td>12.0000 13.0034</td>
<td>98.91 1.09</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>(^{14}\text{N}) (^{15}\text{N})</td>
<td>14 15</td>
<td>14.0031 15.0001</td>
<td>99.6 0.37</td>
</tr>
<tr>
<td>Oxygen</td>
<td>(^{16}\text{O}) (^{17}\text{O}) (^{18}\text{O})</td>
<td>16 17 18</td>
<td>15.9949 16.9991 17.9992</td>
<td>99.76 0.037 0.20</td>
</tr>
<tr>
<td>Fluorine</td>
<td>F</td>
<td>19</td>
<td>18.9984</td>
<td>100</td>
</tr>
<tr>
<td>Silicon</td>
<td>(^{28}\text{Si}) (^{29}\text{Si}) (^{30}\text{Si})</td>
<td>28 29 30</td>
<td>27.9769 28.9765 29.9738</td>
<td>92.28 4.70 3.02</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>P</td>
<td>31</td>
<td>30.9738</td>
<td>100</td>
</tr>
<tr>
<td>Sulphur</td>
<td>(^{32}\text{S}) (^{33}\text{S}) (^{34}\text{S})</td>
<td>32 33 34</td>
<td>31.9721 32.9715 33.9679</td>
<td>95.02 0.74 4.22</td>
</tr>
<tr>
<td>Chlorine</td>
<td>(^{35}\text{Cl}) (^{37}\text{Cl})</td>
<td>35 37</td>
<td>34.9689 36.9659</td>
<td>75.77 24.23</td>
</tr>
<tr>
<td>Bromine</td>
<td>(^{79}\text{Br}) (^{81}\text{Br})</td>
<td>79 81</td>
<td>78.9183 80.9163</td>
<td>50.5 49.5</td>
</tr>
<tr>
<td>Iodine</td>
<td>I</td>
<td>127</td>
<td>126.9045</td>
<td>100</td>
</tr>
</tbody>
</table>
Interpreting MS

1. Check the M+2 region of the spectrum
   The only elements to give significant M + 2 peaks are Cl and Br. If there is no large M + 2 peak then there is no Cl or Br! (remember S ….it is “small”)

2. Is the mass of the molecular ion odd or even?
   Apply the Nitrogen Rule:
   a. if a compound has zero or an even number of nitrogen atoms, its molecular ion will appear as a even m/z value
   b. If it has an odd number of nitrogen atoms, its molecular ion will appear as an odd m/z value
To attain high efficiency of molecular ion formation and give reproducible mass spectra, it is common to use electrons with energies of approximately 70 eV (1600 kcal/mol).

This energy is sufficient not only to dislodge one or more electrons from a molecule, but also to cause extensive fragmentation.

These fragments may be unstable as well and, in turn, break apart to even smaller fragments.
Fragmentation of a molecular ion, $M$, produces a radical and a cation. Only the cation is detected by MS.

\[
\begin{align*}
[A-B]^+ & \rightarrow A \cdot \text{(Radical)} + B^+ \text{ (Cation)} \\
& \rightarrow A^+ \text{ (Cation)} + \cdot B \text{ (Radical)}
\end{align*}
\]
Fragmentation of M

- The chemistry of ion fragmentation can be understood in terms of the formation and relative stabilities of carbocations in solution.

- When fragmentation occurs to form new cations, the mode that gives the most stable cation is favored.
Fragmentation of M

- The probability of fragmentation to form new carbocations increases in the order

\[ \text{CH}_3^+ < 1^\circ < 2^\circ < 3^\circ \]

Increasing carbocation stability
Alkanes

- Fragmentation tends to occur in the middle of unbranched chains rather than at the ends.

- The difference in energy between allylic, benzylic, 3°, 2°, 1°, and methyl cations is much greater than the difference among comparable radicals.

  - where alternative modes of fragmentation are possible, the more stable carbocation tends to form in preference to the more stable radical.
When the weakened bond breaks, one fragment retains the single electron (becoming neutral) and the other must therefore accept the positive charge.

\[
\text{[CH}_3\text{CH}_2\text{CH}_2\text{CH}_3\text{]}^+ \quad \rightarrow \quad \begin{cases} 
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3\text{}^+ \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3\text{}^+ \\
\end{cases} 
\]

How the molecule actually fragments will depend on the stabilities of the individual pieces formed.

Detectable by Mass Spec
Mass Spectrometry

The pentane molecular ion can split in several ways:

- The carbon C2-C3 bond is broken
  - \[ \text{[CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3]^+ \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2^+ + \text{CH}_3\text{CH}_2 \]  
  - \( m/z = 72 \)
  - \( m/z = 43 \)

- The carbon C1-C2 bond is broken
  - \[ \text{[CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3]^+ \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^+ + \cdot\text{CH}_3 \]  
  - \( m/z = 57 \)
  - \( m/z = 15 \)

In each bond breaking case above, the positive charge may reside on either of the fragments:

- The \( m/z \) values for each positive fragment can be determined
- A line representing that fragment is usually found on the mass spectrum and its abundance can be observed

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Mass Spectrometry

- Will one of these bonds break more easily?
- The relative abundances indicate higher amounts of the fragments $m/z = 29$ and $43$, and lesser amounts of the fragments $m/z = 15$ and $57$
  - This indicates that the C2-C3 bond is more likely to break
- In this case, the increased stability of the resulting C2-C3 radicals/ cations drives the fragmentation at this carbon bond
Mass spectrum of 2,2,4-trimethylpentane

Mass spectrum showing the relative abundance of various mass-to-charge ratios (m/z) for the compound 2,2,4-trimethylpentane. The molecular weight (MW) is 114, and the spectrum includes peaks for different fragmentation ions such as [CH₂=CHCH₂]⁺, [CH₃CH₂]⁺, and [CH₃CH₃]⁺.
Alkenes

- Alkenes characteristically show a strong molecular ion peak
- They cleave readily to form resonance-stabilized allylic cations

\[
[\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_3]^+ \rightarrow \text{CH}_2=\text{CHCH}_2^+ + \cdot \text{CH}_2\text{CH}_3
\]
Mass spectrum of 1-butene

\[
\text{CH}_2\text{CHCH}_2\text{CH}_3
\quad \text{MW} = 56
\]

\[
[\text{CH}_2\text{=CHCH}_2]^+ \quad \text{M (56)}
\]
Alkynes typically show a strong molecular ion peak.

They cleave readily to form the resonance-stabilized propargyl cation or a substituted propargyl cation.

\[
\begin{align*}
\text{HC≡CCH}_2^+ & \quad \leftrightarrow \\
\text{HC} = \text{C}=\text{CH}_2^+ & \\
\text{resonance-stabilized propargyl cation}
\end{align*}
\]
Mass spectrum of 1-pentyne

HC≡CCH₂CH₂CH₃
MW = 68

[HC≡CCH₂]⁺

[CH₃CH₂]⁺

m/z

Relative Abundance

M (68)