Week 2

Spectrometry

2.1 Office Hours (Snyder)

- Does cyclohexane only have one ^{13}C NMR signal, and only one ^{1}H NMR signal?

    - 1 singlet for ^{13}C.
    - 1 singlet for ^{1}H.
    - We don't integrate carbon.
    - We only integrate to compare things.
    - We won't have to deal with cyclohexane conformations wrt. NMR on any test.

- What do we need to know about the Karplus correlation?

    - We won't need it for problems.
    - It's useful, but we've got other things to worry about.

- Do chemists/when do chemists run ^{13}C NMR experiments with all carbons isotopically carbon-13?

- Is the reason we don't integrate carbon because the placing of the carbon-13s is random? Would the proportions not still be representative?

- For ^{1}H NMR, feel free to draw in the hydrogen atoms on the line-angle structure.

- Multiplying $n + 1$ of different types of neighbors (e.g., if a hydrogen has 3 neighboring hydrogens to one side and 2 neighboring hydrogens to the other side, it has a maximum of $(3 + 1)(2 + 1) = 12$ peaks in its signal).

    - The multiplication analysis applies only to chains that are completely different.

2.2 Chapter 9: Nuclear Magnetic Resonance and Mass Spectroscopy

From Solomons et al. (2016).

- **Mass spectrometry**: The formation of ions in a mass spectrometer followed by separation and detection of the ions according to mass and charge.

- **Mass spectrum**: A graph that on the x-axis represents the formula weights of the detected ions, and on the y-axis represents the abundance of each detected ion.

    - The x-axis is labeled m/z where m is mass and z is charge.
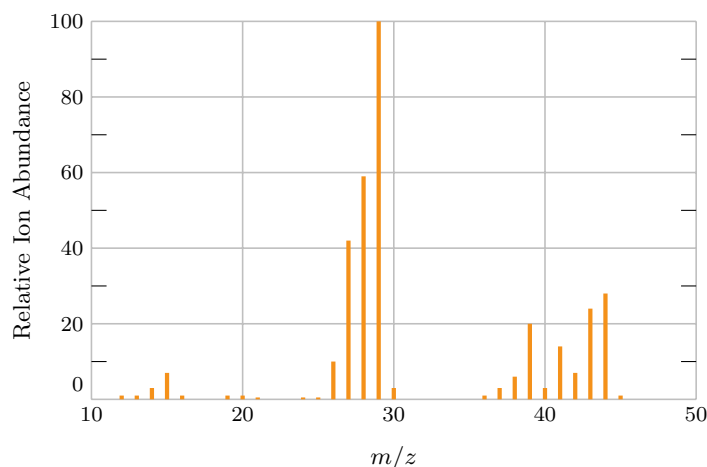
Figure 2.1: The mass spectrum of propane.

- The examples Solomons et al. (2016) consider all have $z = +1$, so the x-axis in them effectively represents the formula weight of each detected ion.

- **Base peak**: The tallest peak in a mass spectrum.

  - Relative ion abundance on the y-axis is either expressed as a percentage of the base peak or directly as the number of detected ions.
  - Usually an easily formed fragment of the original compound.
  - The base peak in Figure 2.1 corresponds to the $C_2H_5{}^+$ ion, $m/z = 29 = 2 \cdot 12 + 5 \cdot 1$.

- **Molecular ion**: The ion with the formula weight of the original compound.

  - One of the higher value m/z peaks.
  - Usually not the base peak.

- Small peaks having m/z values 1 or 2 higher than the formula weight of the compound are due to ^{13}C and other isotopes.

- **Electron impact**: A method for ionizing molecules in a mass spectrometer by placing the sample under high vacuum and bombarding it with a beam of high-energy electrons. *Also known as* **EI**.

  - The energy of the electrons is in the range of $70\,\text{eV}$ or $6.7 \times 10^3\,\text{kJ/mol}$.
  - The incoming electrons ionize the molecules to molecular ions, which are radical cations since they have a +1 charge and an unshared electron.

- Note that there are ionization methods other than EI, but it is the most common.

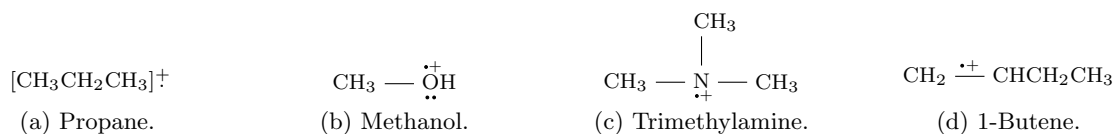- Localizing the radical and charge along the structure.

$[CH_3CH_2CH_3]^{+}$

(a) Propane.

$CH_3 - \overset{\bullet+}{\underset{\bullet\bullet}{O}}H$

(b) Methanol.

$CH_3 - \overset{\displaystyle CH_3}{\underset{\bullet+}{N}} - CH_3$

(c) Trimethylamine.

$CH_2 \overset{\bullet+}{=} CHCH_2CH_3$

(d) 1-Butene.

Figure 2.2: Molecular ions.

- The choice of where we localize the radical/charge is often arbitrary (esp. with hydrocarbons).

- However, "as we might expect, ionization potentials indicate that in [the] formation of radical cations, the nonbonding electrons of nitrogen, oxygen, and halogen atoms, and the π electrons of alkenes and aromatic molecules, are held more loosely than the electrons of carbon-carbon and carbon-hydrogen σ bonds" (Solomons et al., 2016, p. 425).

- Thus, "when a molecule contains oxygen, nitrogen, or a π bond, we place the odd electron and charge at a nitrogen, oxygen, halogen, or π bond. If resonance is possible, the radical cation may be delocalized" (Solomons et al., 2016, p. 425).

- Three important principles.

  1. The reactions that take place are all unimolecular since the pressure is kept so low.

  2. Single-barbed arrows denote the movement of single electrons.

  3. The relative ion abundances give key information about the structures of the fragments produced and their original locations in the molecule.

- Fragmentation by cleavage at a single bond.

  - When such a process happens in a molecular ion, a cation and a radical are produced, although only the cation will be detected by the positive ion mass spectrometers we're considering.

  - Each cleavage can happen in two ways (since one fragment will take the radical and the other will take the positive charge).

  - The path that produces the more stable carbocation will occur more rapidly.

    - Notice the difference in relative ion abundance between the secondary $CH_3CH_2{}^+$ ($m/z = 29$) and the primary $CH_3{}^+$ ($m/z = 15$) in Figure 2.1.

- When drawing cleavage reactions, use brackets and delocalization; when drawing cleavage mechanisms, use localization.

- Chain branching increases the likelihood of cleavage at a branch point because a more stable carbocation can result.

- Examples of fragmentation to form resonance-stabilized cations.

  1. Alkenes ionize and frequently undergo fragmentations that yield resonance-stabilized allylic cations.
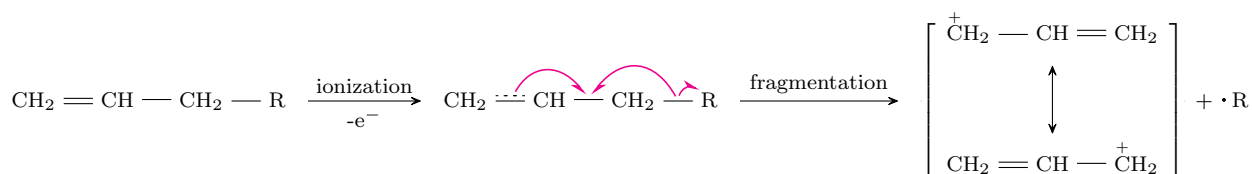

Figure 2.3: Resonance fragmentation: Alkenes.

  2. Carbon-carbon bonds next to an atom with a lone pair usually break readily because the resulting carbocation is resonance stabilized.
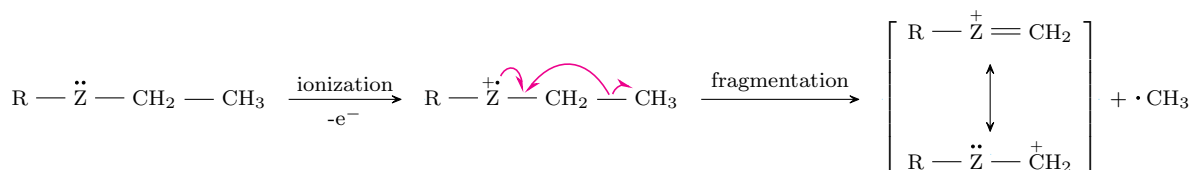

Figure 2.4: Resonance fragmentation: Lone pairs.

3. Carbon-carbon bonds next to the carbonyl group of an aldehyde or ketone break readily because resonance-stabilized ions called **acylium ions** are produced.
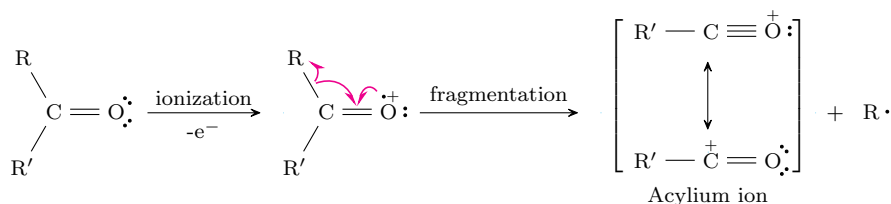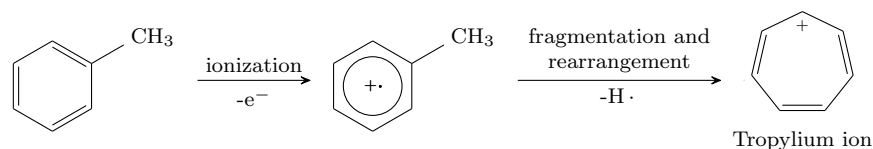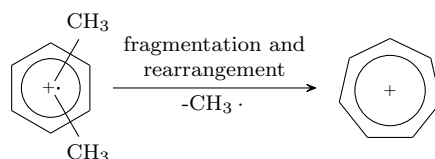

Figure 2.5: Resonance fragmentation: Carbonyls.

   – Note that either the C–R or the C–R′ bond could break.

4. Alkyl substituted benzenes ionize by loss of a π electron and undergo loss of a hydrogen atom or methyl group to yield the relatively stable **tropylium ion**. This fragmentation gives a prominent peak (sometimes the base peak) at $m/z = 91$.

(a) Losing a hydrogen radical.

(b) Losing a methyl radical.

Figure 2.6: Resonance fragmentation: Alkyl-substituted benzene rings.

5. Monosubstituted benzenes with other than alkyl groups also ionize by loss of a π electron and then lose their substituent to yield a phenyl cation with $m/z = 77$.
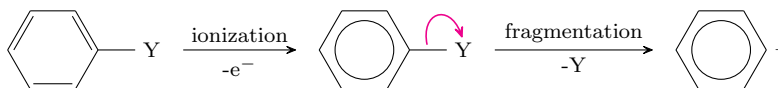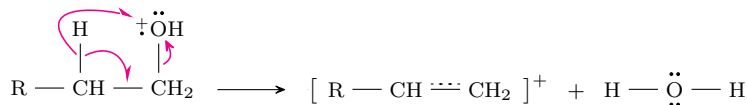

Figure 2.7: Resonance fragmentation: Monosubstituted benzene rings with nonalkyl groups.

   – Y is a halogen, nitro group, acyl group, nitrile group, etc.

• Fragmentation by cleavage of two bonds leads to a new radical cation and a neutral molecule.

1. Alcohols frequently show a peak at $\text{M}^{+\cdot} - 18$. This corresponds to the loss of a molecule of water.

Figure 2.8: Fragmentation: Loss of H_2O.

2. Carbonyl compounds with a hydrogen on their γ carbon undergo a fragmentation called the McLafferty rearrangement.
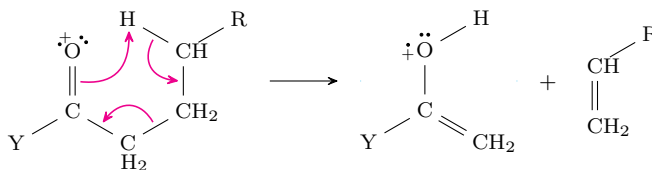

Figure 2.9: Fragmentation: McLafferty rearrangement.

   – Y may be an alkyl, hydride, ether, hydroxyl, etc.

3. There are also often peaks corresponding to the elimination of other small molecules.

• Isotope effects:

   – The presence of ^{13}C will provide a small peak at $M^{+}_{\cdot} + 1$.

   – "In the mass spectrum for a sample containing chlorine, we would expect to find peaks separated by two mass units, in an approximately $3 : 1$ ($75.5\% : 24.5\%$) ratio for the molecular ion or any fragments that contain chlorine" (Solomons et al., 2016, p. 432).

   – "In the mass spectrum for a sample containing bromine, we would expect to find peaks separated by two mass units in an approximately $1 : 1$ ratio ($50.5\% : 49.5\%$ ^{79}Br to ^{81}Br)" (Solomons et al., 2016, p. 433).

   – In a molecule containing two bromine atoms, for example, we'll see peaks at $M^{+}_{\cdot}$, $M^{+}_{\cdot} + 2$, and $M^{+}_{\cdot} + 4$ in a $1 : 2 : 1$ ratio.