

19.2: SPECTROSCOPY OF KETONES AND ALDEHYDES

IR SPECTRA

The carbonyl stretching vibration band C=O of saturated aliphatic ketones appears:

C=O stretch

- aliphatic ketones 1715 cm^{-1}
- alpha, beta-unsaturated ketones $1685\text{-}1666\text{ cm}^{-1}$

Figure 8. shows the spectrum of 2-butanone. This is a saturated ketone, and the C=O band appears at 1715 .

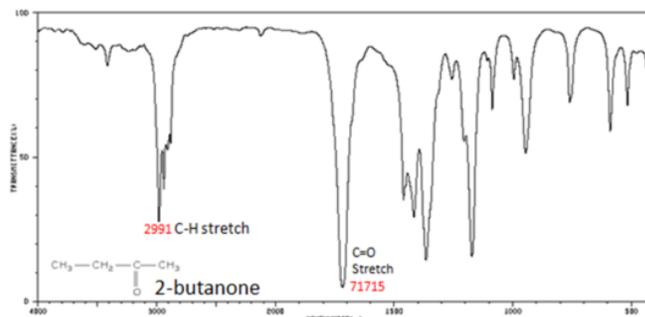


Figure 8. Infrared Spectrum of 2-Butanone

If a compound is suspected to be an aldehyde, a peak always appears around 2720 cm^{-1} which often appears as a shoulder-type peak just to the right of the alkyl C-H stretches.

H-C=O stretch $2830\text{-}2695\text{ cm}^{-1}$

C=O stretch

- aliphatic aldehydes $1740\text{-}1720\text{ cm}^{-1}$
- alpha, beta-unsaturated aldehydes $1710\text{-}1685\text{ cm}^{-1}$

Figure 9. shows the spectrum of butyraldehyde.

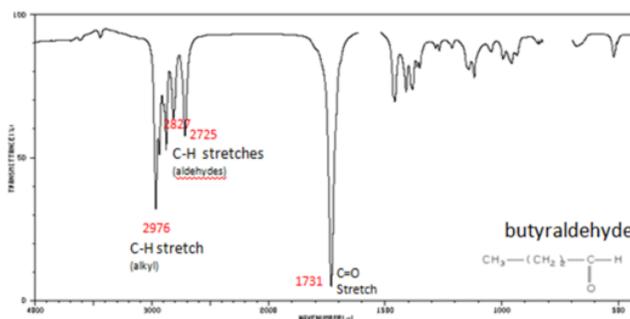
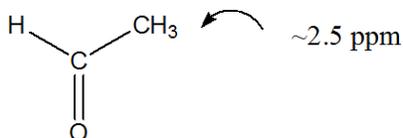


Figure 9. Infrared Spectrum of Butyraldehyde

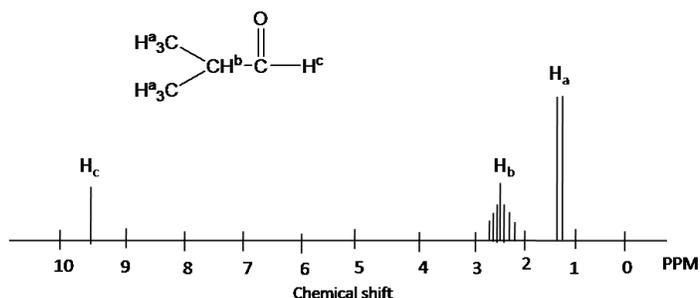
NMR SPECTRA

Hydrogens attached to carbon adjacent to the sp^2 hybridized carbon in aldehydes and ketones usually show up 2.0-2.5 ppm.



Aldehyde hydrogens are highly deshielded and appear far downfield as 9-10 ppm.

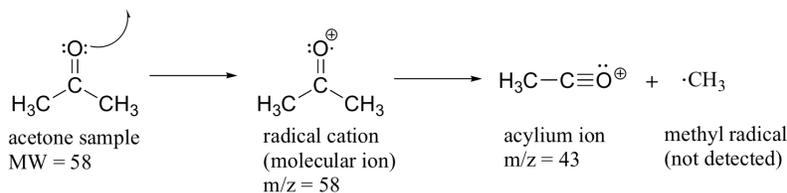
Chemical shift of each protons is predicted by ^1H chemical shift ranges (H_a): chemical shift of methyl groups (1.1 ppm). (H_b) The chemical shift of the -CH- group move downfield due to effect an adjacent aldehyde group: (2.4 ppm). The chemical shift of aldehyde hydrogen is highly deshielded (9.6 ppm).



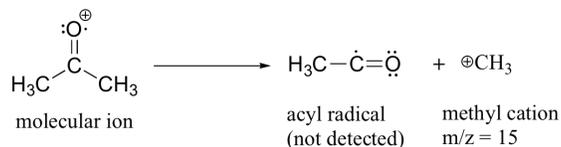
4) Splitting pattern is determined by $(N+1)$ rule: H_a is split into two peaks by H_b (#of proton=1). H_b has the septet pattern by H_a (#of proton=6). H_c has one peak. (Note that H_c has doublet pattern by H_b due to vicinal proton-proton coupling.)

MASS SPECTRA

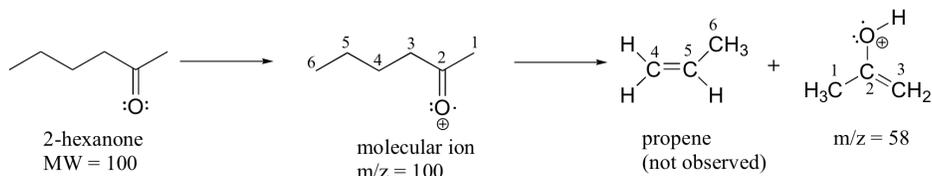
Much of the utility in electron-ionization MS comes from the fact that the radical cations generated in the electron-bombardment process tend to fragment in predictable ways. Detailed analysis of the typical fragmentation patterns of different functional groups is beyond the scope of this text, but it 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 $m/z = 43$. 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 $m/z = 43$) and a methyl radical, which is neutral and therefore not detected.



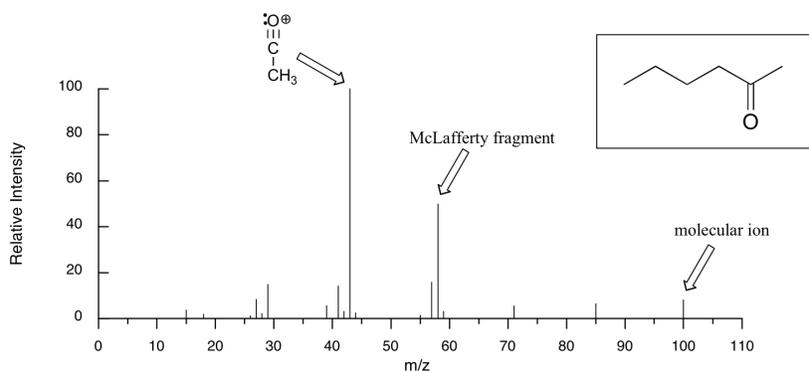
After the parent peak and the base peak, the next largest peak, at a relative abundance of 23%, is at $m/z = 15$. This, as you might expect, is the result of formation of a methyl cation, in addition to an acyl radical (which is neutral and not detected).



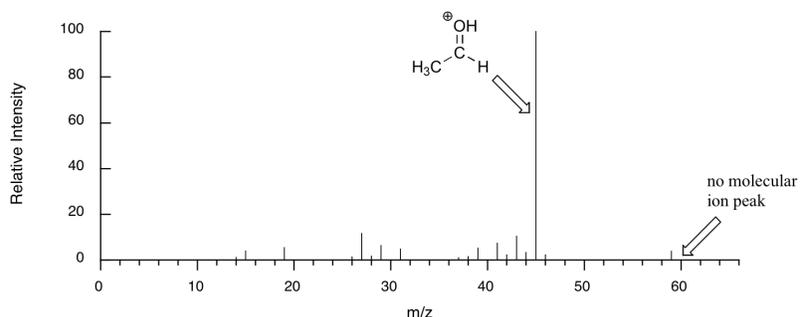
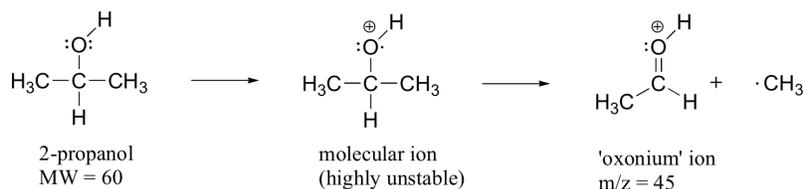
A common fragmentation pattern for larger carbonyl compounds is called the **McLafferty rearrangement**:



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.

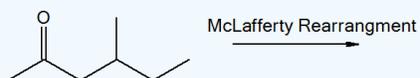
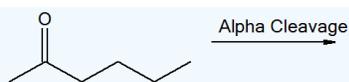


Other functional groups have predictable fragmentation patterns as well. By carefully analyzing the fragmentation information that a mass spectrum provides, a knowledgeable spectrometrist can often 'put the puzzle together' and make some very confident predictions about the structure of the starting 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.

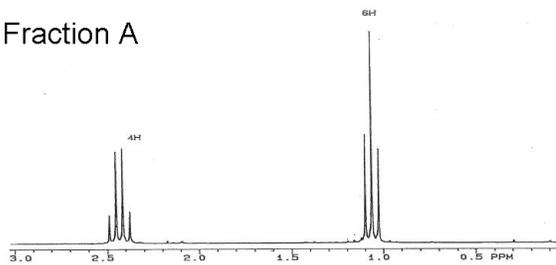
Exercise

1. a) What are the masses of all the components in the following fragmentation reactions?

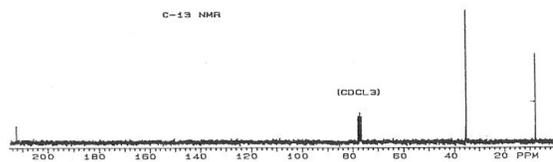


b) A mixture was separated into three fractions: A, B, and C. Elemental analysis reveals that the fractions are structural isomers with the following composition: 69.72% C, 11.70% H, and 18.58% O. The IR spectra for all fractions show several moderate bands around 2950 cm^{-1} , and a strong band near 1700 cm^{-1} . The proton and ^{13}C NMR spectra for each fraction are shown below. Give the common name and draw the bond-line structure for each fraction and correlate the NMR signals with their respective atoms.

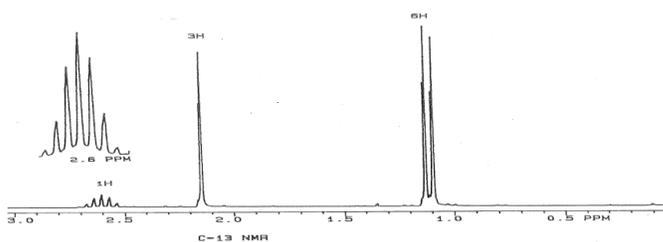
Fraction A



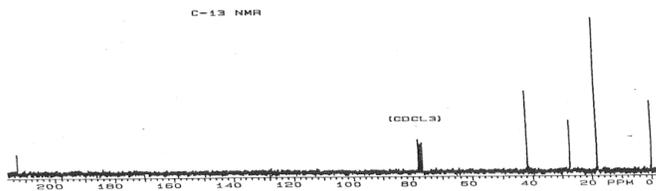
C-13 NMR



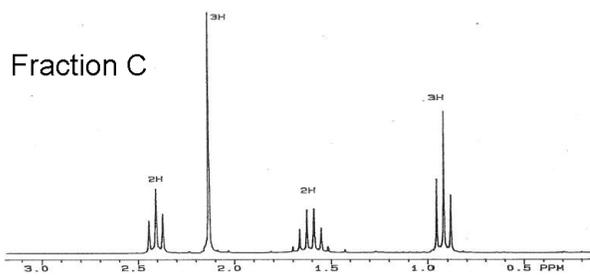
Fraction B



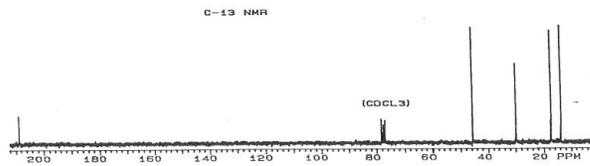
C-13 NMR



Fraction C

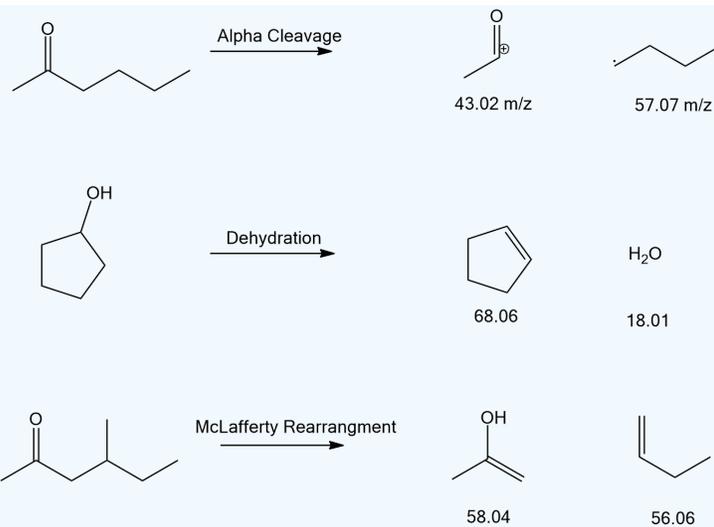


C-13 NMR

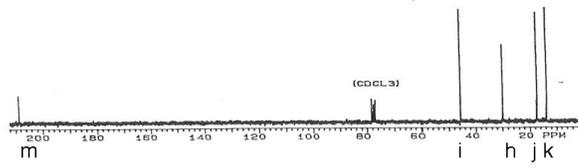
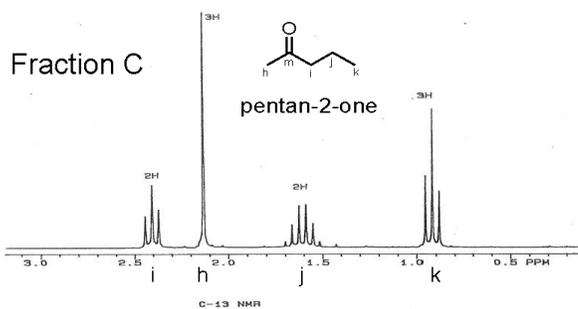
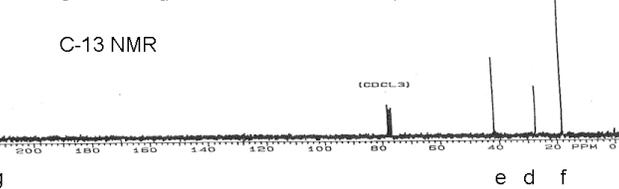
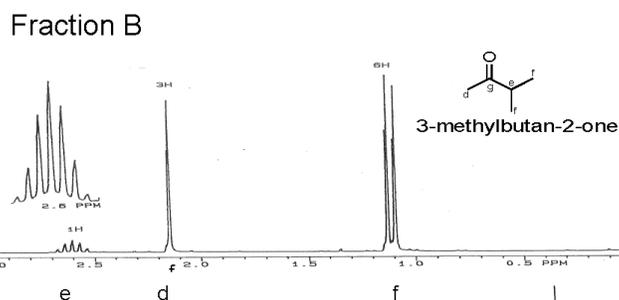
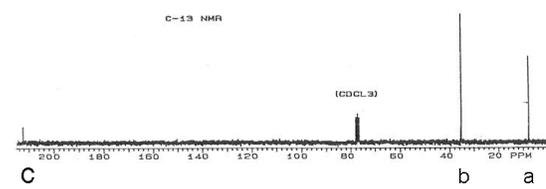
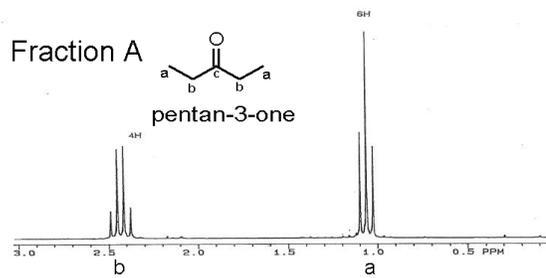


Answer

1. a)



b)



CONTRIBUTORS AND ATTRIBUTIONS

- [Dr. Dietmar Kennepohl](#) FCIC (Professor of Chemistry, [Athabasca University](#))
- Prof. Steven Farmer ([Sonoma State University](#))
- [Organic Chemistry With a Biological Emphasis](#) by [Tim Soderberg](#) (University of Minnesota, Morris)
- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)

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