

INTRODUCTION TO ORGANIC CHEMISTRY



UNIT 05: Structure Determination

- **Quantitative analysis**

We can assume that carbon and hydrogen will be present in all organic compounds. Carbon and hydrogen can be quantitatively determined via a reaction with dry oxygen in a combustion reaction, and use of an empirical formula.

Task 5a

When 4-ketopentenoic acid is analyzed by combustion, it is found that a 0.3000 g sample produces 0.579 g of CO₂ and 0.142 g of H₂O. The acid contains only carbon, hydrogen, and oxygen. What is the empirical formula of the acid?

- **Qualitative analysis**

Chemical tests can be used to reveal the presence of many functional groups.

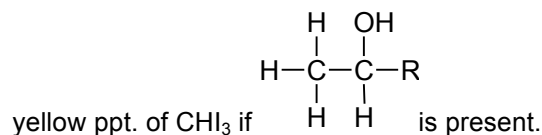
Alkenes

1. with potassium manganate (VII). Color change from purple to colorless.
2. with bromine. Color change from orange/brown to colorless.

Alcohols

1. with PCl₅. Dense white, steamy fumes of HCl liberated, can be confirmed by production of dense white fumes with NH_{3(aq)} (test for -OH group).
2. with Na metal. Hydrogen will be liberated. Test for Hydrogen with lighted splint, squeaky pop.
3. with a carboxylic acid and concentrated sulfuric acid. This will yield an ester that is characterized by a fruity smell.

4. the triiodomethane (iodoform) reaction. Addition of I_2 and warm NaOH will yield a distinctive

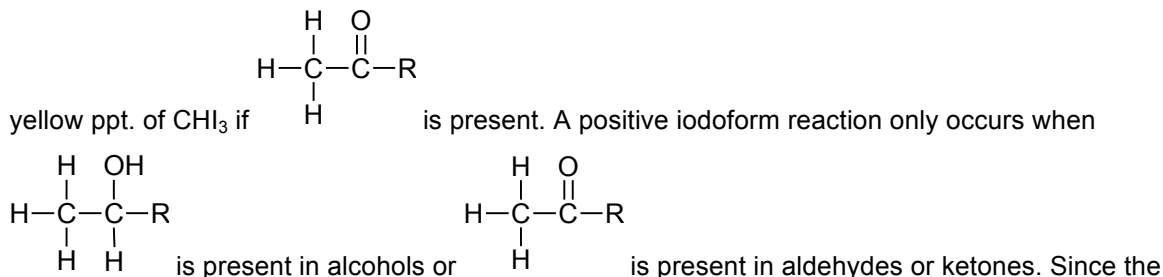


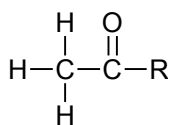
Aldehydes and Ketones

- with 2,4 dinitrophenylhydrazine (Brady's reagent). Addition will yield an orange/yellow ppt. 2,4-dinitrophenylhydrazine is converted to the corresponding 2,4-dinitrophenylhydrazone on reaction with aldehydes & ketones. These hydrazones are colored solids and have very specific melting points. Purification of them, finding a melting point and then a comparison with a known value, can lead to the specific identification of the original aldehyde or ketone. Suppose for example a distinction is required between pentanal (b.p. 104°C) and pentan-2-one (b.p. 102°C). A boiling point comparison would be inconclusive since they are so close. However a firm identification is possible by producing the 2,4-DNP derivatives and comparing their melting points, pentanal-2,4-dinitrophenylhydrazone (98°C) and pentan-2-one-2,4-dinitrophenylhydrazone (141°C).
- with Fehling's solution (Cu (II)) and heat. Aldehydes act as reducing agents giving a color change from blue to red ppt. of Cu (I). In the process the aldehyde is oxidized. No change with ketones.
- with Tollen's reagent (ammoniacal silver nitrate, Ag (I)). Aldehydes act as reducing agents giving a silver mirror of Ag (0). In the process the aldehyde is oxidized. No change with ketones. With Fehling's and Tollen's reagents the reducing hydrogen in the aldehyde causes the color change. Ketones have no such reducing power and so no change is observed. Tollen's reagent contains Ag^+ ions which are readily reduced by the H in the aldehyde to give Ag^0 i.e. Ag metal, a silver mirror. In the process the aldehyde is oxidized.

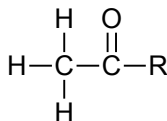


4. the triiodomethane (iodoform) reaction. Addition of I_2 and warm NaOH will yield a distinctive

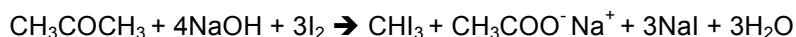




only aldehyde with present is ethanol, it is the only one to give a positive test.



However many ketones contain the group and hence many give a positive test. e.g. propanone warmed with iodine in NaOH. CHI_3 (Triiodomethane/Iodoform) is a yellow ppt, which has an "antiseptic" smell).



Task 5b

1. Draw formulae for the following alcohols and state which ones undergo a positive triiodomethane test.

Methanol, ethanol, propan-1-ol, propan-2-ol 2-methylpropan-2-ol

2. Which of the following pairs could be distinguished using only the triiodomethane reaction?

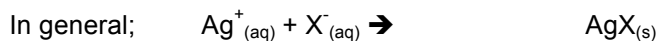
- (a) ethanol and propan-2-ol
- (b) methanol and propan-1-ol
- (c) propan-1-ol and propan-2-ol
- (d) $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}_3$ and ethanol
- (e) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ and methanol

Carboxylic acids

1. with PCl_5 . Dense white, steamy fumes of HCl liberated, can be confirmed by production of dense white fumes with $\text{NH}_{3(\text{aq})}$ (Test for -OH group).
2. with sodium hydrogen carbonate or sodium carbonate. Will yield carbon dioxide. Test for carbon dioxide will turn limewater cloudy.
3. with an alcohol and concentrated sulfuric acid. This will yield an ester that is characterized by a fruity smell.

4. Halogens in organic compounds

1. add aqueous NaOH. This releases the halide ion into solution. Acidify with dilute nitric acid then the halide ion can then be detected using aqueous silver nitrate and aqueous ammonia.



AgF is soluble, the other silver halides being insoluble with the following colors;

AgCl white
 AgBr cream
 AgI pale yellow

It is obvious that these colors are very similar and as such can it can be difficult to distinguish between them. Further identification can be sought by the use of ammonia.

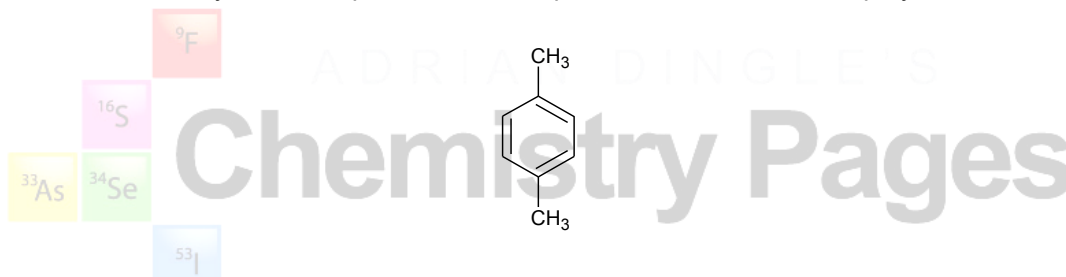
Precipitate	With dilute ammonia	With concentrated ammonia
AgCl	Completely dissolves to form soluble $[\text{Ag}(\text{NH}_3)_2]^+_{(aq)}$	Completely dissolves
AgBr	Partially dissolves	Completely dissolves
AgI	Insoluble	Insoluble

- **Physical methods of structure determination**

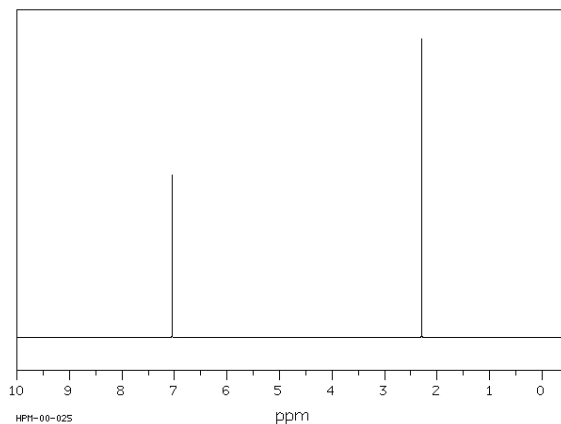
^1H Nuclear Magnetic Resonance Spectroscopy (^1H NMR)

^1H NMR spectra are obtained by exposing very small samples of material to radiofrequencies. The sample is dissolved in an inert solvent (that does not contain H nuclei) and a reference material. The nuclei are exposed to the radio frequencies between the poles of a strong magnet, and eventually an energy that corresponds to the exact energy gap between a higher and lower energy state (the higher and lower energy states are ones where the nuclei are either aligned with or against the magnetic field) will be achieved. At this point the nuclei absorb the energy, “flip”, and are said to be in resonance with the applied frequency, hence the term “nuclear magnetic resonance”. These absorptions can be detected and recorded by the spectrometer and hard copy spectra are printed.

Nuclei will flip their spins at different points according to their chemical and electronic environment. This means that different compounds containing different “types” of H nuclei will yield different patterns of absorption and hence very different spectra. For example consider the molecule p-xylene.



This molecule has two different “types” of H nuclei. Those on the CH₃ groups, and those directly connected to the aromatic ring. Thus we would expect two peaks in the spectrum to show these two different types of hydrogen atoms. The spectrum is shown below.

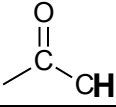
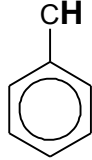
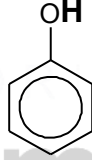
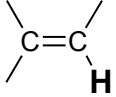
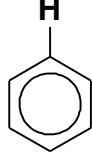
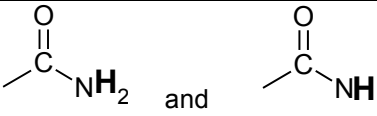
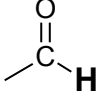
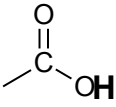


Source: SDBSWeb: <http://riodb01.ibase.aist.go.jp/sdbs/>
(National Institute of Advanced Industrial Science and Technology, June 2008)

Points to note.

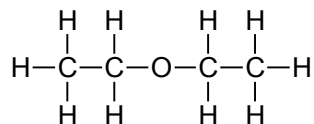
1. A reference compound is used so that the peaks of the molecule being tested are seen relative to that compound (0 on the scale above). Tetramethylsilane ((CH₃)₄Si) is a popular choice as is CDCl₃. TMS is particularly attractive as it has all twelve of its H's equivalent so it only gives one sharp peak which serves as the reference point, it is inert, has a low boiling point so it can be removed from the sample at the end of the procedure, and its peak appears relatively high in the field so it can easily be distinguished from the other peaks. The TMS peak at 0 has been omitted from the spectrum above.
2. The x-axis plots δ values that are the chemical shift values away from the reference compound.
3. The integrated areas of the peaks show the relative abundance. In this case, the peak at δ 2.30 is in a ratio of 6:4 with the peak at δ 7.10. This is consistent with six, methyl hydrogen atoms and four, aromatic hydrogen atoms.
4. Electronegativity causes a downfield shift.
5. Hydrogen atoms attached to a carbon atom that is part of a multiple bond or aromatic ring appear downfield of those that are attached to saturated C atoms.

Typical shifts of hydrogen atoms in certain environments are shown in the table below. These peaks are relative to TMS and should only be used as a *guide* since solvents and different environments can cause significant shifts. N-H and O-H bonds are particularly susceptible to such shifts and changes.

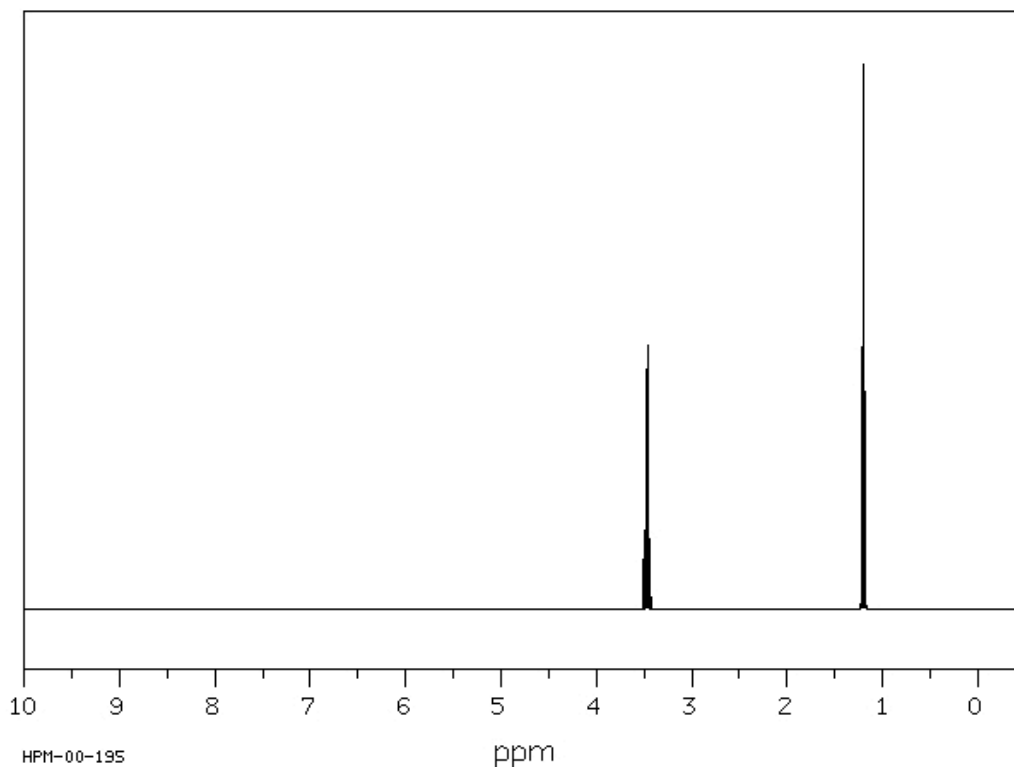
H environment	δ /ppm shift
R-CH	0.8 – 2.0
N-H and O-H	1.0 – 5.5
	2.0 – 3.0
N-CH	2.3 – 3.0
	2.3 - 2.6
Cl-CH and Br-CH	3.0 – 4.2
	4.5 – 10.0
O-CH	3.2 – 4.2
	4.5 – 6.0
	6.5 – 8.0
	5.0 – 12.0
	9.0-10.0
	11-12

Spin-Spin Splitting

Most organic compounds will yield spectra that are significantly more complex than those that just showing single peaks (singlets). For example, consider the spectrum of diethyl ether.



Here there is a set of four (a quartet) around δ 3.4 and a set of three (a triplet) around δ 1.2. (*These are NOT easy to see with the naked eye, but you should be able to determine that the peaks are not singlets*).



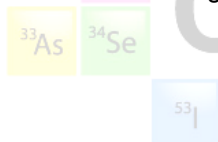
Source: SDBSWeb: <http://riodb01.ibase.aist.go.jp/sdbs/>
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The data below show the actual values for each of the peaks in the quartet and the triplet.

	Hz	ppm	Intensity
QUARTET	1052.16	3.507	161
	1045.16	3.484	490
	1038.17	3.461	501
	1031.17	3.437	171
TRIPLET	368.77	1.229	509
	361.78	1.206	1000
	354.78	1.183	487

The peaks at δ 1.10 and δ 3.40, in the ratio 3:2 (6:4) are largely what we would expect from a compound that has $\text{CH}_3\text{-C}$ hydrogen's and $\text{-CH}_2\text{-O}$ hydrogen's in the ratio 6:4, but why are the peaks not singlets?

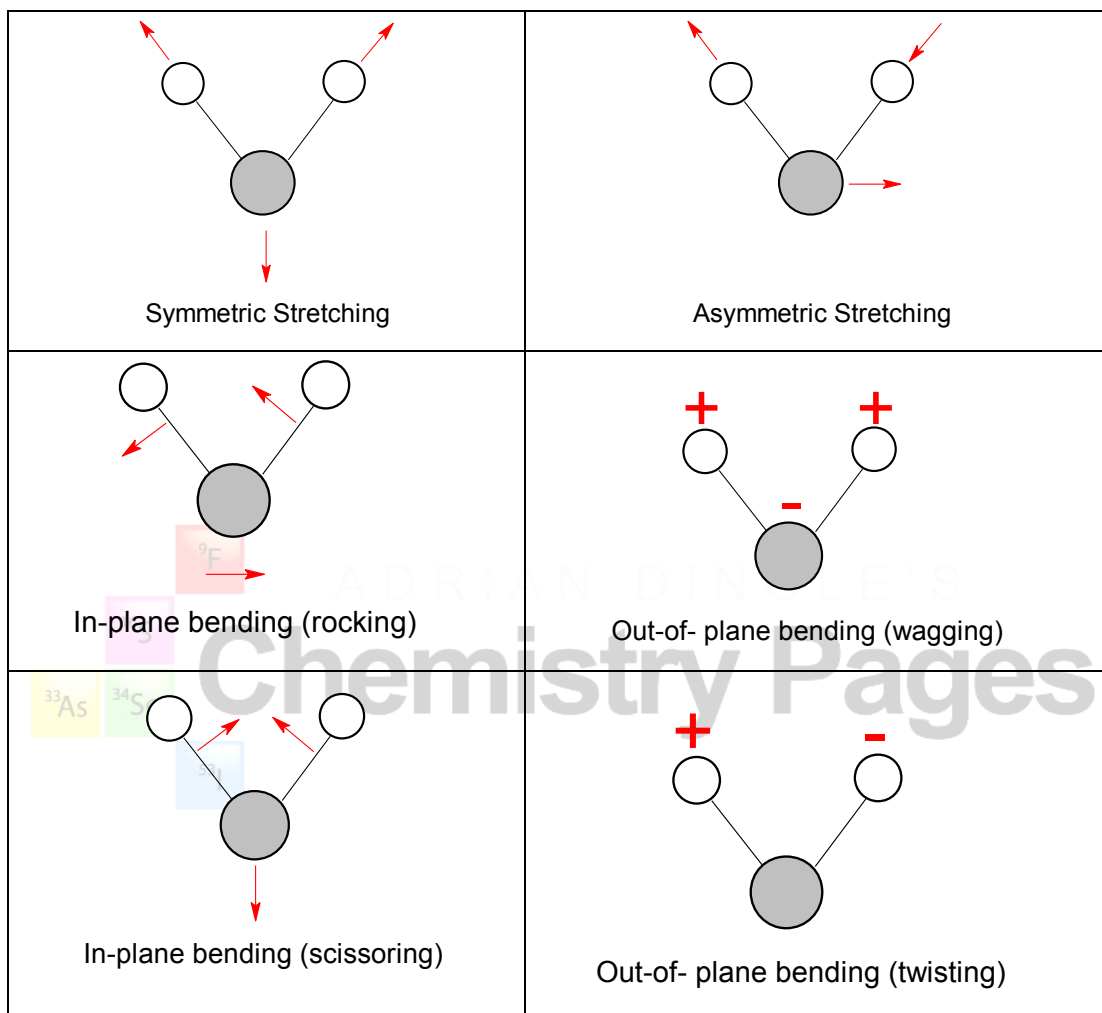
The methyl signal is split into a triplet with relative abundance 1:2:1 and the CH_2 signal is split into a quartet with relative abundance 1:3:3:1. We can predict the splitting pattern using the $n+1$ rule. Simply stated, if a hydrogen atom has n hydrogen atom neighbors, then its signal will be split into $n+1$ peaks. Hydrogen atoms that are chemically equivalent DO NOT split one another. Extra complex patterns can be observed when adjacent hydrogen atoms have nearly the same, but not identical, shifts. Hydrogen atoms that split one another's signals are said to be 'coupled'.



Chemistry Pages

Infrared Spectroscopy

When they are exposed to infrared radiation of a particular frequency, covalent bonds will absorb that radiation and consequently bend and stretch. (+ means coming towards the reader, - moving away).



An infrared spectrometer will record these absorptions and produce a chart that can be analyzed to help identify the bonds present. There are two different areas of importance on these IR spectra. Firstly there are the functional group bands. These bands will appear in the same place for compounds that have the same, particular functional groups regardless of the detail of the molecular structure. Some typical bands are listed below.

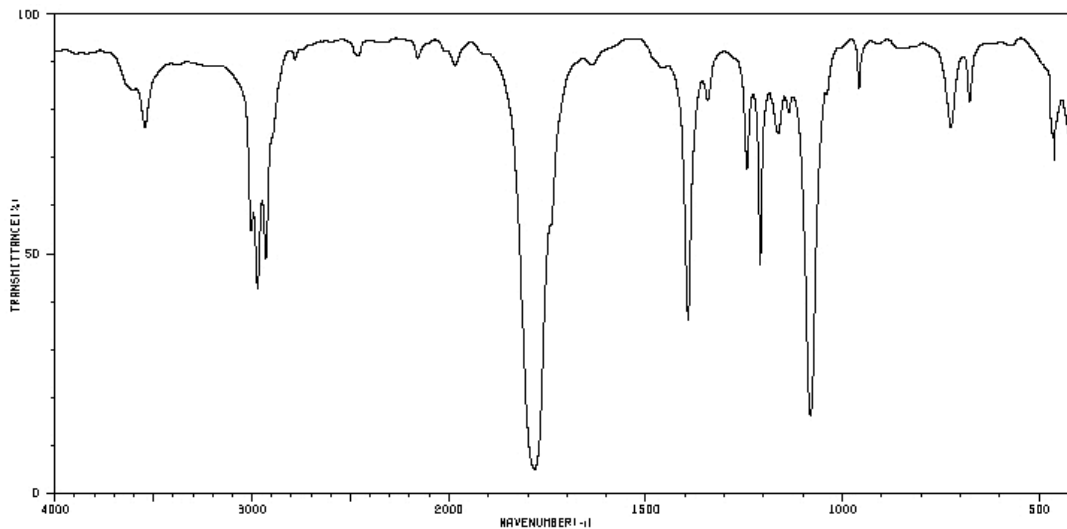
Bond	Location	Frequency Range cm^{-1}
C-H	Various	2850 - 3100
C-O	Alcohols, esters and carboxylic acids	1000-1300
O-H	Alcohols	3200 - 3550 (broad peaks due to H-bonds)
O-H	Carboxylic acids	2500 – 3300 (broad peaks due to H-bonds)
N-H	Amines and amides	3200 - 3500
C=O	Aldehydes, ketones, esters, acids and amides	1640 - 1750

The second part of the spectrum is the fingerprint region. As the name suggests this area is unique to each individual compound and is made up from the unique bending and stretching combinations of each compound. The fingerprint region is located at lower frequencies, typically $700\text{-}1500\text{ cm}^{-1}$.



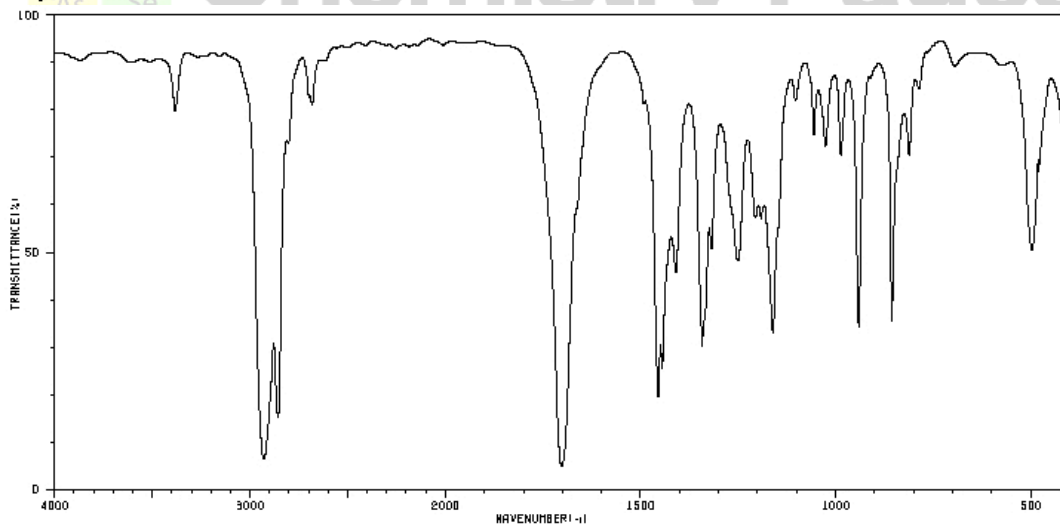
For example, cyclobutanone shows bands at approx. 3000 cm^{-1} (C-H), and 1780 cm^{-1} (C=O) and a complex fingerprint region. Cycloheptanone shows similar (C-H) and (C=O) bands (as one would expect) but a different fingerprint region (also as expected).

Cyclobutanone



Source: SDBSWeb: <http://riodb01.ibase.aist.go.jp/sdbs/>
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Cycloheptanone



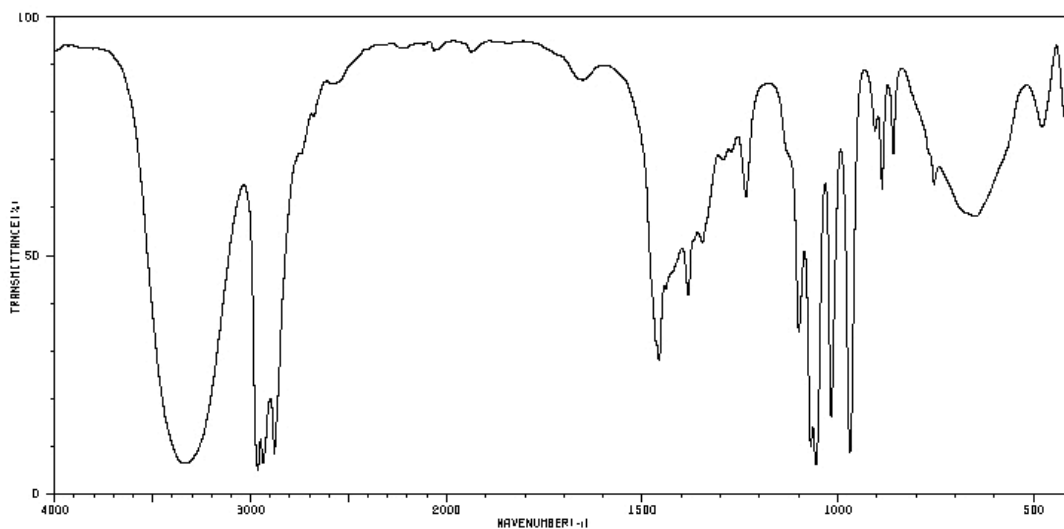
Source: SDBSWeb: <http://riodb01.ibase.aist.go.jp/sdbs/>
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By comparing the spectra obtained from an unknown sample to one created from a known sample, deductions can be made about the type of bonds present in the unknown.

Task 5c

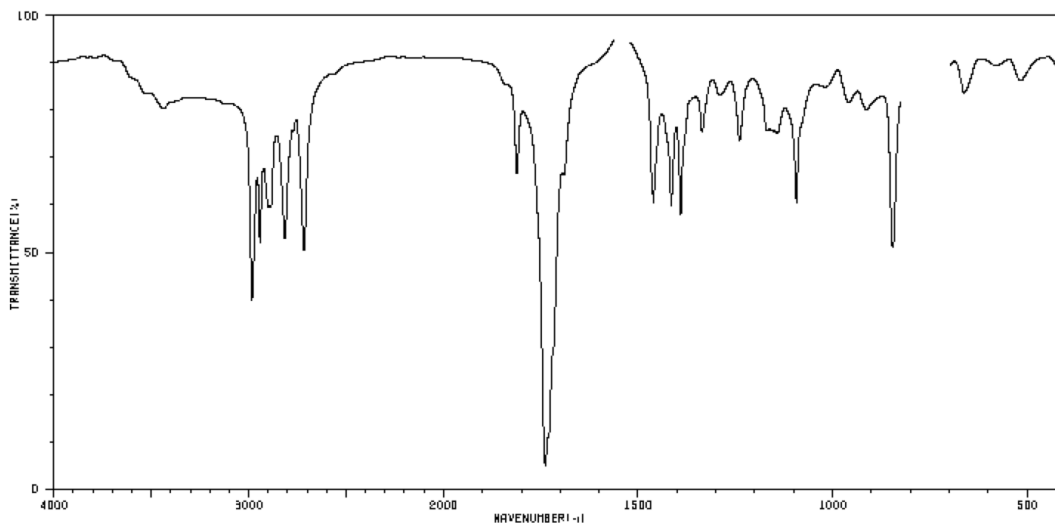
Compound P, C_3H_8O , can be converted to compound Q, C_3H_6O . Q gives a positive Fehling's test. On treating Q with acidified $Na_2Cr_2O_7$, compound R is formed. R has the molecular formula $C_3H_6O_2$ and is weakly acidic. Suggest names and structures for P, Q and R and interpret the infrared spectra as far as possible and draw the infrared spectra you would expect for compound R.

P



Source: SDBSWeb: <http://riodb01.ibase.aist.go.jp/sdbs/>
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Q



Source: SDBSWeb: <http://riodb01.ibase.aist.go.jp/sdbs/>
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Mass Spectrometry

In a mass spectrometer an ionizing beam of electrons has enough energy to remove electrons from molecules to produce positive ions and to split a molecule into fragments. The spectrometer then sorts the fragments according to their mass-charge ratio (m/z), and determines the relative abundance of each ion. A hard copy spectrum is produced by the machine.

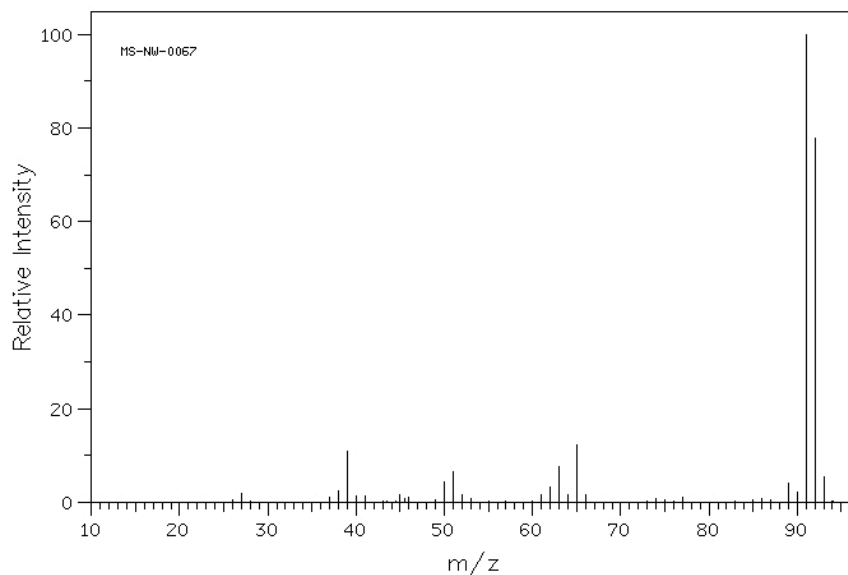
The molecule with just one electron removed is called the molecular ion or parent ion. Often, mass spectra will show peaks that are equal to $[M+1]^+$. These peaks are caused by the C^{13} isotope that occurs naturally and will have an intensity around 1.1% times the number of carbons present relative to the $[M]^+$ peak. Other isotopes such as Cl^{35} and Cl^{37} can also provide useful data. A compound containing one chlorine atom will show two parent ions peaks, two units apart, in the ratio of 75:25, the naturally occurring abundances of Cl^{35} to Cl^{37} .

Fragments that result from the collapse of the parent ion are called daughter ions. For example, the mass spectrum for methanol shows peaks at 32, 31, 29 and 28. These correspond to the ions $[CH_3OH]^+$ (molecular or parent ion), and the daughter ions $[CH_3O]^+$, $[CHO]^+$ and $[CO]^+$. Assigning the peaks to different fragments of a molecule can give clues about its structure.



Task 5d

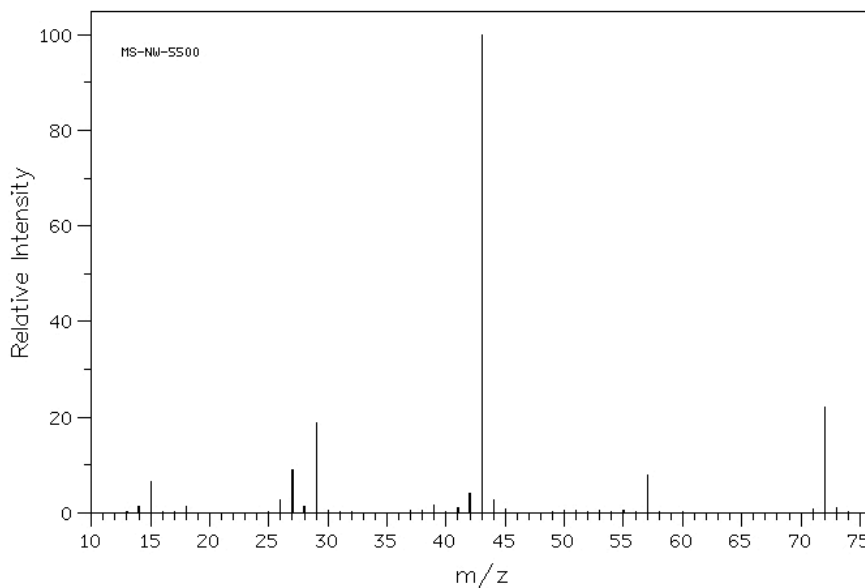
1. The mass spectra for methylbenzene is shown below. Identify the peaks at m/z 91, 92 and 93 in the spectrum. Identify the main fragmentation process.



Source: SDBSWeb: <http://riodb01.ibase.aist.go.jp/sdbs/>

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2. The mass spectra for butanone is shown below. Identify the peaks at m/z 72, 43 and 29 in the spectrum. Identify the main fragmentation process.



Source: SDBSWeb: <http://riodb01.ibase.aist.go.jp/sdbs/>

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