EXPERIMENT 7
INFRARED SPECTROMETRY OF
4-tert-BUTYLCYCLOHEXANONE AND 4-tert-BUTYLCYCLOHEXANOL:

TECHNIQUES: IR

This week you will obtain the IR spectra of your products from week 5 and 6.

READING ASSIGNMENT:

➢ Background handout
➢ This handout for procedure on operating the IR and additional background on IR spectroscopy at the end of the handout
➢ Technique 20: Infrared Spectroscopy in techniques in Organic Chemistry 3rd Ed.
➢ Supplementary information in Janice Gorzynski Smith (2nd ed), Chapter 13

EXPERIMENTAL NOTES:

Obtain IR spectra for your products from Weeks 5 and 6. Analyze the IR spectra to confirm the identity and determine the purity of your products from each experiment.

IMPORTANT SAFETY INFORMATION

4-tert-butylicyclohexanol and 4-tert-butylicyclohexanone are irritants! Wear gloves when working with either of them!
Dichloromethane is toxic. Avoid contact and inhalation.

Operation of the IR Spectrophotometer:

➢ To obtain a background:
   1) Mount one clean salt plate on the sample holder (Handle the salt plates only by the edges.)
   2) Press the “scan” button or followed by “background” and then “execute”. The instrument will automatically obtain the background spectrum.

➢ To obtain a IR spectrum for your sample:
   3) Remove the salt plate and prepare your sample by adding one drop of the liquid unknowns using a boiling stick. For solids use a KBr salt plate, a solution in DCM, or Nujol. See background handout for details!
   4) Mount the salt plates containing sample on the sample holder (Handle the salt plates only by the edges.)
   5) Press the “execute” button or “scan” followed by 4. The instrument will automatically obtain the spectrum over the full wavelength range of the instrument within a short period of time.

➢ To manipulate your spectrum use the arrow keys on the keyboard. For horizontal manipulation of the spectrum use the following buttons:
“↩” shifts the spectrum to the left while “→” shifts the spectrum to the right
“<>” expands the spectrum and “> <” contracts the spectrum
There are four analogous buttons available for vertical manipulation of the spectrum

- **Note:** if there is a vertical black line on the screen the buttons described above will not work properly. Press the “Shift” key followed by the “→” key to get rid of the line and be able to set your spectrum.

- A good spectrum should be in the range of ~4000 cm\(^{-1}\) to ~600 cm\(^{-1}\). You should see an uninterrupted line for the spectrum and the peaks should all be fully visible on the screen.

- To mark your peaks:
  1) Press the “Shift” key followed by the “→” key to get the peak-picking line and be able to mark your peaks.
  2) Once the line is on the screen, to mark a particular peak you press the “Shift” and “<>” keys
  3) To move on to the next peak you want to mark use the “→” and “↩” keys as necessary.
  4) Once you’re done marking peaks press the “Shift” key followed by the “→” key to get rid of the peak-picking line.

- Readjust your spectrum using the arrow keys and once it’s all ready, to obtain a print-out of your spectrum press “Plot” to print. (Note: the “Print” button should NEVER be used!!)

- Remove the salt plates and clean them with methylene chloride and Kim-Wipes. Keep the plates away from water! Return the salt plates to the desiccator for storage.

**While you are waiting to obtain you spectra or if you are finished with time to spare, work on the Sapling spectroscopy dry lab assignment in class!**
BACKGROUND:

A chemical bond can be compared to a coiled spring. Just as it takes energy to stretch a spring, energy is needed to stretch a chemical bond. A bond stretches and contracts as it vibrates. The frequency of molecular vibrations of organic molecules lies in the infrared region of the electromagnetic spectrum. Infrared light activates these vibrations, a process that consumes energy. In IR spectroscopy, a sample of a molecule is irradiated with light in the IR portion of the electromagnetic spectrum. The energy of the infrared radiation after it has passed through the sample is then measured. A decrease in the energy of a particular wavelength indicates that the molecule has absorbed this energy by undergoing some type of vibration. The energy of the transmitted radiation is plotted as a function of the frequency of the infrared radiation. The plot appears as a series of peaks and is called an infrared spectrum.

Each of these peaks indicates a particular type of vibration that the molecule is experiencing when that frequency of radiation is absorbed. Some of these peaks represent vibrations of the molecule as a whole, but some of them represent vibrations of only particular parts of the molecule. Functional groups tend to absorb at predictable regions of the spectrum. The vibrations of functional groups are so characteristic that a quick glance at an infrared spectrum can give immediate information about the functional groups present in that molecule. The particular frequency of vibration often allows distinctions to be made between functional groups having very similar structures. For example, IR spectroscopy allows one to distinguish between aldehydes, ketones, esters, anhydrides, acid chlorides, etc., all of which are carbonyl-containing compounds.

The frequency of the radiation is conveniently expressed by most chemists in wave numbers, (cm\(^{-1}\)), a unit which is proportional to the energy of the infrared radiation. The higher the wave number, the greater the energy of radiation needed to activate the vibration. The infrared spectrum normally covered is from \(4000 \text{ cm}^{-1}\) to about \(650 \text{ cm}^{-1}\). The functional group region, however, extends from \(4000 \text{ cm}^{-1}\) to about \(1500 \text{ cm}^{-1}\). It is in this region that we look for those frequencies that are characteristic of particular functional groups. The \(1500 \text{ cm}^{-1}\) to \(650 \text{ cm}^{-1}\) region is called the fingerprint region and is used most often for comparison purposes. With some exceptions, no two compounds have identical infrared spectra. Thus, if one wants to verify the structure of a particular compound, a comparison of the infrared spectrum of the compound with the infrared spectrum of the known structure will provide this information. The stronger the bond, the higher the frequency of vibration. Triple bonds are stronger than double or single bonds between the same two atoms and have higher frequencies of vibration. Thus, the C-C single bond in ethane, the C=C double bond in ethene, and the C=C triple bond in ethyne vibrate about \(3.6 \times 10^{13}\), \(5.0 \times 10^{13}\), and \(6.5 \times 10^{13}\) times/second, respectively. Meanwhile, the C-O single bond in ethanol (CH3CH2-OH) and the C=O double bond in acetaldehyde vibrate about \(3.1 \times 10^{13}\) and \(5.2 \times 10^{13}\) times/second, respectively. The stronger the bond, the more energy is needed to stretch the chemical bond. The frequency of bond vibration is proportional to the energy associated with the vibration, as given by the equation \(E=\hbar \nu\).
Hybridization affects the bond lengths, and bond strength. Bonds are stronger in the order $sp > sp^2 > sp^3$, and the observed frequencies of C-H vibration illustrate this nicely.

<table>
<thead>
<tr>
<th>Hybridization</th>
<th>Frequency (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$sp$</td>
<td>3300</td>
</tr>
<tr>
<td>$sp^2$</td>
<td>3100</td>
</tr>
<tr>
<td>$sp^3$</td>
<td>3000</td>
</tr>
</tbody>
</table>

As the atom bonded to carbon increases in mass, the frequency of vibration decreases (wavenumber gets smaller):

<table>
<thead>
<tr>
<th>Atom</th>
<th>Frequency (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H</td>
<td>3000</td>
</tr>
<tr>
<td>C-C</td>
<td>1200</td>
</tr>
<tr>
<td>C-O</td>
<td>1100</td>
</tr>
<tr>
<td>C-Cl</td>
<td>750</td>
</tr>
<tr>
<td>C-Br</td>
<td>600</td>
</tr>
<tr>
<td>C-I</td>
<td>500</td>
</tr>
</tbody>
</table>

**Resonance Contributors and the Relative Vibrational Frequencies for C=O Bonds**

In order to determine the relative vibrational frequencies for C=O bonds in different compounds, you may be able to estimate their relative strengths using resonance theory. For example, suppose the carbonyl carbon in a compound is attached to some atom or group, $Y$, giving the compound the general formula RCO$Y$. Such a compound will have at least two resonance contributors. When $Y$ has a lone pair (as in carboxylic acids, esters, amides, and acid halides), three resonance structure are possible: A, B, and C. When $Y$ has no lone pair (as in aldehydes and ketones), only two resonance structures are possible: V & X.

The actual structure of the molecule is neither A nor B nor C (V nor X), but the combination of A, B, & C or V & X in a single structure which is represented by the resonance hybrid (composite structure) shown. The strength of the C=O bond depends on the relative contribution (importance) of the resonance structures. If A, B, & C (or V & X) were of equal importance, the C=O bond of the hybrid would be two parts single bond and one part double bond (or halfway
between a double bond and a single bond). This “1/3 double bond (or 1/2 double bond)” would be weaker than a double bond, but stronger than a single bond. Therefore, the bond would vibrate at a lower frequency.

There are two factors to consider:

1. **As Y become more electronegative**, resonance structure B (X) will be less important because the electronegative Y withdraws electrons from the positively charged carbon, making B (X) less stable. Resonance structure C will also be less important because the positive charge will be on the electronegative element Y. Therefore, as Y becomes more electronegative, resonance structure A (V) is more important, and the carbonyl will have more double bond character, and therefore, will vibrate at a higher frequency.

2. **As the ability of Y to donate its electrons increases**, resonance structure C becomes more important. One way to measure how well Y donates its electrons is to look at the basicity of Y. Basicity increases to the left in any row of the periodic table, and increases as you move up any column. The more basic the atom is, the more willing it is to donate its electrons.

Comparing an ester, for example, \( Y = O \) with an amide \( Y = N \), nitrogen is more basic and, therefore, has a greater ability donate its electrons. So the resonance structure C will be much more important. **Result:** the C=O will have less double bond character, and will therefore vibrate at a lower frequency. **Conclusion: An amide will absorb at a lower frequency than an ester.**

**Amide:** Resonance structure C is important because N likes to donate its electrons.

**Ester:** Resonance structure C is less important because O is less basic than N and therefore not as willing to donate its electrons.
Note: We can also use the electronegativity argument to compare an ester and an amide. Comparing an ester with an amide, $O$ is more electronegative than $N$. An electronegative oxygen destabilizes resonance structure $B$ and $C$, giving the $C=O$ more double bond character. An ester will therefore absorb at a higher frequency than an amide. This is the same conclusion we reached above. *What is the actual frequency of the carbonyl of an amide vs. the carbonyl of an ester?*

Amide $C=O$: 1650 cm$^{-1}$
Ester $C=O$: 1725-1750 cm$^{-1}$

If $Y$ is an unsaturated group, such as a vinyl group ($\text{CH}_2=\text{CH}$), an additional resonance contributor, $C$ can be drawn. $B$ and $C$ are important resonance contributors because they are allylic cations. This will give the $C=O$ less double-bond character, therefore, it will absorb at a lower frequency.

*What is the actual frequency of an $a,b$-unsaturated ketone, vs. a regular ketone?*

ketone $C=O$: ~1710 cm$^{-1}$

$a,b$-unsaturated ketone $C=O$: ~1680 cm$^{-1}$

The application of resonance theory to the determination of the structure of carbonyl compounds will only provide relative frequencies. It will help us to arrange the assigned compounds in order of their $C=O$ vibrational frequencies but it will not allow us to determine actual frequencies.

**Taking an IR Spectrum:**

In order to determine the infrared spectrum of a compound, one must use a sample holder or cell. Since glass and plastics (materials that consist of covalent bonds) absorb strongly throughout the infrared region of the spectrum, metal halides such as sodium chloride or potassium bromide are used. Single crystals of NaCl or KBr are cut and polished to give salt plates that are transparent throughout the IR region and used to fabricate cells that can hold liquid samples.

Salt Plates are made of NaCl and, therefore, are sensitive to moisture and are easily cracked. Atmospheric moisture, as well as moisture in a sample, causes the polished plate surface to become pitted and fogged. Fogged plates scatter and reflect infrared radiation instead of transmitting it efficiently; poor-quality spectra are the result. Fogged plates may also retain
traces of compounds from previous runs, giving rise to false peaks. Fogged plates can be polished by rubbing them with circular motion on an ethanol-water saturated paper towel laid on a hard surface. (Only TA’s are authorized to polish salt plates – don’t try it yourself!)

Clean the salt plates by rinsing with couple drops of dichloromethane followed by wiping off the solvent with a dry tissue. Handle the plates only by the edges, never by their flat surfaces, because oil and moisture from your fingers will leave fingerprints that absorb in the IR region of the spectrum. The plates must be stored in a desiccator when not in use.

**For Liquid Samples:** Add a drop of liquid (or ½ drop if the liquid is nonvolatile) to the surface of one plate, and then place the second plate on top causing the liquid to spread out to form a thin film between the two plates. Mount the plates on the sample holder and determine the spectrum according to the instructions provided by your TA. A spectrum determined by this method is referred to as a neat spectrum. The plates should be touched only on their edges. Be certain to use a sample that is dry and free from moisture. Few problems are encountered in thin-film sampling, and these are easily solved. Too much liquid between the plates causes leakage around the edges of the plates and gives rise to a spectrum in which many of the peaks are too strong. To remove the excess liquid, wipe part of the sample off the plates (gently) with a dry tissue. Too little sample between the plates results in a spectrum with weak peaks. More sample may be added to the plates and the spectrum rerun.

**For Solid Samples:** Three methods are widely used in organic solid samples. The first method is to make a thin film. A small amount of solid sample is dissolved in dichloromethane and is then applied to the middle of the salt plate, and the CH₂Cl₂ is allowed to evaporate. This method does not work for all solid samples. The second method is to make a Nujol mull. A small amount of solid sample is ground to a fine powder and the powder is mixed with a drop of Nujol to make a mull. The third method is to make a KBr pellet. The solid sample is mixed with KBr powder in mortar and pestle, and the resulting mixture is placed in a press. Making successful KBr pellets requires some skill and practice.

**The IR Spectrum: What to look for when examining IR spectra**

An infrared spectrometer determines the position and relative sizes of all the absorptions (bands or peaks) in the infrared region and plots them on a piece of paper. This plot of % transmittance versus wavenumber is referred to as the infrared spectrum of the compound. Depending on the functional groups present in the molecule, the spectrum exhibits many strong, medium, and weak absorption bands between 4000 cm⁻¹ and 600 cm⁻¹. Take notice of frequencies at which an absorption occurs, shapes, and intensities for characteristic bands in the spectrum. The eye must be trained to recognize these features using the IR correlation chart (Table 18.2, pp. 245-247 and other tables). Often, when reading the literature of organic chemistry, you will find absorption referred to as strong (s), medium (m), weak (w), broad, or sharp. The author is trying to convey some idea of what the peak looks like without actually drawing the spectrum. You will practice the same for your IR analysis of your unknowns in this experiment.