Acid and Base Catalyzed Esterification

Background

Carboxylic acids react with alcohols to form compounds known as esters (R represents any hydrocarbon group):

\[
\text{RCOOH} + \text{HO-} \text{R'} \rightleftharpoons \text{RCOOR'} + \text{H}_2\text{O}
\]

This acid-catalyzed equilibrium synthesis was developed by Emil Fischer (1852-1919). There are other pathways for making esters but this one is simple and interesting for reasons beyond the utility of making new compounds.

Esters are very common organic compounds. Typically we associate these substances with aromas and flavor essences. For example, ethyl butanoate:

\[
\text{CH}_2\text{CH}_2\text{C}_3\text{O}\text{OCH}_2\text{CH}_3
\]

is one of the esters associated with the flavor and aroma of pineapples. The actual constituents of flavor and aroma in foods are many and not static. Over 50 esters have been identified among the volatile compounds found in Bartlett pears [a personal favorite]. As the chemical processes associated with ripening take place, the mix of chemicals also changes. This is one of the reasons why "artificial" flavorings never measure up to the real thing. It is neither cost effective nor entirely possible to recreate the subtle blend in natural foodstuffs.

The prevalence (and importance) of esters goes far beyond making things smell and taste good [and yes, some esters smell and taste very nasty]. Fats and oils are also esters. These are composed of the triol glycerol, and long-chain "fatty" acids:

In these compounds the esterification reaction occurs at each alcohol site and thus involves three acids (which may or may not be the same):

Adapted from: Vial Organic, Tom Russo and Mark Meszaros
Waxes likewise are esters of long-chain alcohols and long-chain acids and there are cyclic esters
called lactones in which a molecule with both alcohol and carboxylic acid functional groups reacts with
itself. Esters are also the units in some types of polymers (hence polyester):

\[
\text{HO\textsubscript{w}OH + CO\textsubscript{w}wCO\textsubscript{OH} \rightarrow H_2O + \text{HO\textsubscript{w}OH} + \text{CO\textsubscript{w}wCO\textsubscript{OH}}} \equiv \text{etc.}
\]

Whatever the type of ester, the basics of the reaction involve a process called condensation in
which a small molecule—in this case water—is split out between two compounds, leaving a linkage to
form a larger molecule from the original units:

\[
\text{R-COOH} + \text{OH}^+ \rightarrow \text{R-COO}^+ \text{H}^+ + \text{H}_2\text{O}
\]

A moment of consideration will lead to the conclusion that this does not seem to make a lot of sense. Carboxylic acids should be proton donors, not acceptors. While the reaction might be boxed otherwise, studies with radioactive oxygen-tagged compounds indicate that this is the correct way in which the linkage forms in the ester.

The proposed mechanism for Fischer esterification involves a process related to nucleophilic substitution. The word "substitution" is clear enough but a nucleophile needs some introduction. Organic chemists use the terms nucleophile and electrophile to describe certain electron-rich and electron-deficient species in a reaction. In terms that are familiar from the study of inorganic reactions, a nucleophile is a Lewis base or a structure with at least one lone pair of electrons. An electrophile, on the other hand, is a Lewis acid or a structure with an incomplete octet or perhaps a positive charge.

Because of their extra electron density, nucleophiles are attracted to parts of molecules with partial positive charges or electron deficiencies (such as sp\(^2\) or sp carbons). Electrophiles are attracted to electron-rich sites such as lone pairs or partial negative charges.

The mechanism of Fischer esterification is not thought to be a true nucleophilic substitution, but it involves a nucleophile (the alcohol) adding to the carboxylic acid and a subsequent elimination step. Initially the carboxylic acid is protonated by the stronger inorganic acid catalyst (typically sulfuric acid):
In the second step the alcohol nucleophile (two lone pairs on the oxygen) adds at the \( sp^2 \) carbon and the alcohol proton is lost:

\[
\begin{align*}
\text{R}_1\text{C} = \text{OH}^+ & \quad \text{OH}^- \\
\text{R}_1\text{O} = \text{H}^+ & \quad \text{R}_2\text{C} = \text{OH}
\end{align*}
\]

This is an important step in the mechanism because it is here that the new ester bond between the carboxyl group carbon and the alcohol oxygen forms. A series of fast equilibrium proton exchanges occur at either of the two acid -OH groups (which are equivalent):

\[
\begin{align*}
\text{R}_1\text{C} = \text{OH} & \quad \text{OH}^- \\
\text{R}_1\text{O} = \text{H}^+ & \quad \text{R}_2\text{C} = \text{OH}_2^-
\end{align*}
\]

Next, water is eliminated at one site or the other:

\[
\begin{align*}
\text{R}_1\text{C} = \text{OH} & \quad \text{OH}_2^- \\
\text{R}_1\text{O} = \text{H}^+ & \quad \text{R}_2\text{C} = \text{OH}^+
\end{align*}
\]

In the final step the excess proton leaves, regenerating the inorganic acid catalyst:

\[
\begin{align*}
\text{R}_1\text{C} = \text{OH}^+ & \quad \text{OH}^- \\
\text{R}_1\text{O} = \text{H}^+ & \quad \text{R}_2\text{C} = \text{O}^-
\end{align*}
\]

Although the uncatalyzed reaction is quite slow (several days at reflux temperatures), Fischer and Speier discovered in 1895 that the addition of only a small amount of mineral acid greatly accelerates the attainment of equilibrium.

Because each of these steps is an equilibrium and the equilibrium constant for many esterifications is less than 10, control of reaction conditions to maximize products is of some importance. Based on LeChâtelier's Principle, we know that increasing the amount of either of the reactants should help. If either the alcohol or acid is considerably less expensive this is one possible approach. Under the right experimental conditions it is also possible to remove water as refluxing is taking place. The disappearance of a product will tend to drive (or pull, if you like) the reaction to the right. However, in laboratory scale organic synthesis the usual aim is not so much getting a lot of product as it is determining how the product forms and how it can be isolated, purified and identified.
The search for alternative fuels is an ongoing research enterprise. The combustion of fossil-based fuels (natural gas, oil, gasoline, petroleum diesel fuel, etc.) is a one-way process which will eventually exhaust the available stocks of raw petroleum materials and add significantly to the amount of carbon dioxide in the atmosphere. The potential consequences of both activities will probably still be argued long after it is too late to do anything about them.

A good alternative fuel would ideally come from renewable resources, be energy-rich, “green” in production (i.e., not produce unwanted or harmful side-products or employ harmful chemicals for synthesis) and be at least “carbon-neutral”. This last requirement means that no new carbon would be released into the environment during combustion. Plant-based fuels meet this criterion because the carbon dioxide which plants consume from the atmosphere is returned when the plant material combuts. If only part of the plant is burned, then the process might actually be better than carbon-neutral, assuming the remaining plant material is used in some other form that sequesters the carbon and prevents its return to the atmosphere, and that manufacturing processes are not fuel-intensive. There are certainly other issues associated with the widespread use of plant-based biofuels, not the least of which is the resources like water and arable land which such crops might take from needed food production.

A lot of attention has been devoted in the popular press recently to a fuel called biodiesel. An internet search under this term will yield a spectacular number of hits that range from government reports to home-brew recipes touted by those who now run their vehicles on fuel they produce from vegetable oil (in some cases, used frying oil from restaurants!). It turns out that biodiesel fuel is amazingly simple to make, rather “green”, and could be carbon-neutral. Its energy content is one of the things this experiment is about.

The diesel engine was designed by Rudolph Diesel in 1895 as an alternative to the standard internal combustion engine that powers most of our cars. It could run on less refined hydrocarbon mixtures that ignite upon compression and therefore required no spark. The first diesel engines were actually designed to run on vegetable oil but petroleum diesel was available as a cheap by-product of gasoline production and was less viscous than vegetable oil so the engines were eventually redesigned for it.

Biodiesel is the methyl (or ethyl) ester of the fatty acids found in vegetable oils or animal fats. At the simplest, these fats are triglycerides. That means some rather large carboxylic acids have formed a triple ester with the glycerol molecule (1,2,3-propanetriol, a tri-alcohol). This makes for a very viscous liquid because the strands of the fat get tangled with each other. To reduce the viscosity it is possible to detach the glycerol molecule and replace it with methanol at each strand of fatty acid. The process is known as transesterification and can be catalyzed by either acid or base. Because potential acid residues are not friendly to metal engine parts and because the process is faster with the base catalyst, sodium or potassium hydroxide is generally used along with methanol to treat the vegetable oil.
The glycerol by-product can be used to produce soap and is also being investigated as an ingredient in animal feedstocks.

The mechanism of the transesterification, which differs significantly from acid-catalyzed Fischer esterification process, is shown below:

\[ \text{H}_3\text{C}^-\text{OH} + \text{OH}^- \rightleftharpoons \text{H}_2\text{C}^-\text{O}^- + \text{H}_2\text{O} \]

In the first step the base catalyst reacts with the alcohol (in this example and your synthesis, methanol) producing an alkoxide ion (CH\textsubscript{3}O\textsuperscript{-}) and a protonated form of the catalyst.

In step 2 the very nucleophilic alkoxide ion attacks each ester linkage to the glycerol backbone at the carbon of the carbonyl group (the more positive end of the polar C=O bond). An intermediate forms which then breaks down in step 3 into a new methyl ester and leaves a glyceride anion.

The protonated form of the catalyst gives back a proton to the negative site in step 4 and both regenerates the catalyst and begins the reconstruction of the glycerol molecule.

This process continues until all three strands from the fat have been converted into simple—if long—methyl esters. The resulting mixture is biodiesel (the glycerol by-product is more dense and eventually separates from the reaction mixture on its own).
Producing small batches of biodiesel for testing is about as simple as combining vegetable oil, methanol, a little KOH and stirring. The reaction can be done easily in a small vial. On standing overnight the glycerol sinks to bottom of the mixture. The final product would normally be washed and dried like the other ester you will be synthesizing, but this processing adds time and little benefit for our purposes.

Determining the energy content of biodiesel means burning it and measuring the heat produced. In the first year course you did an experiment comparing the heats of combustion of hexane, heptane and octane. The same apparatus (nested metal cans and small fuel burners with wicks) will give acceptable results for this experiment.

You will be using the CBL temperature probe so be sure to bring your TI-83/84 calculator to class and have the HCHEM.83G programs installed. Octane, with a known heat of combustion, can be used to determine the calorimeter constant of the apparatus and then the biodiesel and standard petroleum diesel can be burned to determine their heats of combustion and compare their combustion characteristics with those of octane (do they burn “clean”?).

Finally, IR and NMR spectra of the starting vegetable oil and a sample of biodiesel and petroleum diesel are provided so you can compare structural elements in the reactant and product.
The Experiment

There are four parts to this experiment:

- synthesis and isolation of an ester
- analysis of the synthesis product by gas chromatography/mass spectrometry
- synthesis of biodiesel from olive oil
- comparing the heat of combustion and burning characteristics of some fuels

The following non-locker materials will be provided:

- concentrated acetic, formic and propanoic acids [fume hood]
- concentrated sulfuric acid [fume hood]
- 1-propanol, 2-propanol, 2-methyl-1-propanol, 3-methyl-1-butanol, 1-pentanol
- micro sample vial with teflon seal
- saturated Na₂CO₃
- anhydrous MgSO₄
- 18 x 150 mm test tube
- beral pipets, pasteur pipet, cotton
- ice
- olive oil
- methanol
- 10 M KOH
- sample vial with teflon seal and stirring flea
- calorimeter apparatus
- fuel burners
- octane
- petroleum diesel fuel

The Chemicals

Formic acid (HCOOH) is a colorless liquid with a pungent odor. It is miscible with water and alcohol. The concentrated liquid is dangerously caustic to skin! It is used as a decalcifier, a reducing agent in dyeing wool fast colors, for tanning and in regenerating old rubber. **Persons with severe allergic reactions to bee stings should handle the liquid with extreme caution.**

Propanoic acid (C₃H₅COOH) or propionic acid is an oily liquid with a slightly pungent and rancid odor. It is used in textile dyeing and as a solvent for cellulose.

Acetic acid (or ethanoic acid) has a pungent odor and in concentrated form (17 M) produces painful burns on the skin. It is soluble in water and is itself an excellent solvent for many organic compounds. While it is a weak acid, concentrated solutions are extremely irritating to tissue, especially mucous membranes. It is used in the manufacture of various acetates including plastics and textiles, in dyeing, preserving foods and in many organic syntheses. Household vinegar is 5% acetic acid. Ingestion of more concentrated solutions may cause severe corrosion of the mouth with vomiting, circulatory collapse and eventual death.
Sulfuric acid is a clear, colorless, oily liquid in concentrated form (98%). It is highly corrosive and has a high affinity for water, abstracting it from wood, paper, sugar, etc., leaving a carbon residue behind. Dilution of concentrated sulfuric acid generates a tremendous amount of heat. Here in the lab your instructor prepares the dilute sulfuric acid you use by pouring the concentrated acid slowly over ice while stirring! Even so, the resulting solution is very warm. As with all acid dilutions, acid is added to water, not the reverse, since the heat generated can boil the water at the point of contact and cause spattering.

Sulfuric acid is used to make fertilizers, explosives, dyes, parchment paper, and glue. It is used, in concentrated form, in automobile batteries as the electrolyte. It is corrosive to all body tissues and contact with eyes may result in total blindness. Ingestion may cause death. Frequent skin contact with dilute solutions may cause dermatitis.

1-propanol (C₃H₇OH) or n-propyl alcohol is a liquid with an alcoholic, slightly stupefying odor. It is miscible with water, ethanol and ether. The compound is used as a solvent for resins and cellulose esters. It may be mildly irritating to the eyes and mucous membranes and have a depressant action similar to ethanol.

2-propanol or isopropyl alcohol is a flammable liquid, miscible with water and common organic solvents. It forms a low-boiling azeotrope with water and can also be used to make low-freezing mixtures (i.e., as an antifreeze). It is a solvent in many quick-drying commercial preparations (inks, shellacs, oils, etc.) and is used as a topical antiseptic in a 70% solution (rubbing alcohol). Ingestion of as little as 100 mL can be fatal.

2-methyl-1-propanol or isobutyl alcohol is a colorless, flammable liquid with an odor similar to 1-pentanol, but weaker. It is soluble in about 20 parts water. The compound is used in the manufacture of esters for fruit flavoring essences and as a solvent in paint and varnish removers. Its toxicity is similar to 1-propanol.

3-methyl-1-butanol or isopentyl alcohol (or isoamyl alcohol) has a characteristic disagreeable odor and a repulsive taste. Vapors are poisonous. It is used as a solvent for fats, resins, etc., in the manufacture of mercury fulminate, artificial silk, lacquers and smokeless powders. Its initial topical toxicity is similar to 1-propanol but higher vapor or liquid concentrations may cause depression and narcosis.

1-pentanol or n-amyl alcohol has a mild, characteristic odor and is only slightly soluble in water. It is used as a solvent in organic syntheses. Irritating to the eyes and respiratory passages, prolonged exposure to the compound can cause giddiness, headache and even delirium.

Sodium carbonate occurs in nature in various mineral forms but much is manufactured by the Solvay process or from brines and alkali lake beds. The dry powder is slightly hygroscopic. Aqueous solutions are strongly basic. It is used in the manufacture of other sodium salts, in glass, soap, as a general cleanser (“washing soda”) and in photography.

Magnesium sulfate occurs in nature as the mineral kieserite. The anhydrous compound is a white powder. The heptahydrate (commonly known as Epsom salts) is slightly efflorescent. It is used in bleaching, the manufacture of mother-of-pearl and frosted papers, for fireproofing and in mineral waters. It has relatively low toxicity. Oral doses as high as 15 grams have been prescribed as a cathartic.
Methanol or methyl alcohol was originally obtained from the destructive distillation of wood (hence its common name of “wood alcohol”) but is now made synthetically on an industrial scale. Unlike its close relative ethanol, methanol is quite toxic and a much better solvent for inorganic salts. Its industrial uses range from an important solvent to raw material for the synthesis of formaldehyde (methanal) and methyl esters. It is also often used to “denature” ethanol, rendering it unfit for human consumption. Methanol burns with a non-luminous bluish flame.

Octane is a clear, colorless and flammable liquid obtained from petroleum. It is a component of commercial gasoline which is a mixture of hydrocarbons in the range of C_4 to C_{12}. The “octane number” of gasoline is actually not related to its octane content (which may be a quite minor constituent). Instead it represents the percentage of “isooctane” (2,2,4-trimethylpentane) which must be blended with heptane in order to obtain the same degree of engine “knock” as the gasoline mixture being tested. “Knock” is the sound produced by an engine when the rate of pressure increase in the cylinder is too great during ignition of the gasoline vapor.

Potassium hydroxide consists of white or slightly yellow pellets or flakes which absorb water and CO_2 rapidly from the air. It is soluble in about 0.9 parts water and dissolves with the liberation of considerable heat. The compound and its solutions are very caustic to tissue. It is used in the manufacture of liquid soaps, in the treatment of cotton for fabrics, in paint and varnish removers and in photoengraving. Ingestion may produce violent pain in throat and eventual collapse. Untreated ingestion may be fatal.

Olive oil is obtained from the fruit of the cultivated olive tree and consists of mixed glycerides of oleic acid (83.5%), palmitic acid (9.4%), linoleic acid (4.0%), stearic acid (2.0%), arachidic acid (0.9%) and other minor constituents. It is used in foods as well as for cooking foods and in the manufacture of soaps, cosmetics and pharmaceutical preparations.

**Technique Discussion**

For the first part of the experiment you will be assigned an acid/alcohol pair from which to synthesize an ester.

Reactions of this sort are often quite slow, even with a catalyst. They are therefore generally refluxed. This means that the vapor is trapped and allowed to condense and drip back into the mixture during a heating period. Generally this is done with a water-jacketed condenser. However, in this experiment since the refluxing temperature is fairly low and the amounts—and therefore the time—are fairly small, a microscale method utilizing a small, sealed vial will be adequate as long as there is no leakage of material during the heating process.

A 250 mL beaker of boiling water [hotplate] should be prepared while the sample is being mixed. About 1 g of the assigned alcohol is placed in the vial and 2.5 mL of the assigned organic acid is added. About 5 drops of concentrated sulfuric acid should be added last (this functions as the catalyst). The vial must then be tightly sealed. Leakage will result in loss of reactants and products and will invalidate yield calculations [not to mention spoiling results]. Masses of the reactants should be recorded [rough balance].

The vial is placed carefully into the boiling water bath and heated for about 25 minutes. A constant tiny stream of bubbles issuing from around the cap is a sign of a leak. If this is caught early the vial can be removed from the bath and the cap tightened.
During the 25 minute heating process the biodiesel synthesis can be set up with a partner. The complete separation of the biodiesel from the glycerol by-product is slow and so the sample will be stored overnight.

The vegetable oil/alcohol/catalyst proportions are somewhat critical at small scale so exercise care when measuring. Too much catalyst will produce some very nice soap, but no biodiesel. Once your regular ester is in the boiling water bath [students should share a hot plate for the boiling water with two 250 mL beakers on it; this leaves a second hot plate to be used for stirring the biodiesel mixture], you can prepare the biodiesel reaction mixture.

Use a graduated beral pipet to measure 5 mL of olive oil into the vial containing a stirring flea. With a second graduated beral pipet add 0.75 mL of methanol to the vial. Finally, carefully add 2 drops of 10 M KOH directly from the dropping bottle. Be sure the bottle is going to behave and not dribble a bunch of drops into the sample before actually placing the vial under it. Cap securely. Mix gently by inverting the vial several times. Do not shake it! Place the vial on its side on a hot plate/stirrer and turn on the stirrer so that the entire contents are mixed [do not heat!]. If it seems like the ends of the vial are being ignored, occasionally pick up the vial and invert it a few times. Mix for 10 minutes.

Place the vial upright in a small beaker and store overnight.

After heating for 25 minutes, the small vial containing the synthesized simple ester and other substances should be placed on the bench to cool to touch. Cooling in an ice/water bath for 3 minutes should reduce any possible pressure buildup and also limit the solubility of the ester in the mixture.

The ester can be roughly separated from the mixture by pouring the contents of the vial into a test tube containing about 8 mL of the ice/water mixture from the cooling bath. The vial should be opened cautiously since there may be residual pressure inside which could cause the contents to spurt out. A small additional rinse of the vial with ice water is advisable. The ester should be more or less water-insoluble while the acid and perhaps the alcohol are more water-soluble. After gentle stirring the ester forms a layer on top of the water and can be carefully removed with a beral pipet.

Depending on the amount of product it may be advisable to use a smaller test tube for the extraction and removal process. A narrower tube will make the ester layer easier to see and separate from the aqueous layer.

Residual alcohol dissolved in the ester may be removed by the cautious addition of about 2 mL of saturated Na₂CO₃. The ester is insoluble in this solution while the alcohol is very soluble. The sodium carbonate should also destroy any acid residue that remains in the sample. The ester phase should again be removed with a clean beral pipet. A small amount of solid MgSO₄ is then added to the ester to dry it. Complete drying may take 3-5 minutes. When drying is complete the liquid should show no sign of cloudiness. Fine suspended crystals of the drying agent may not be visible but they will jam (and ruin) the chromatography syringes if there are not removed. The dried ester should therefore be filtered through cotton packed into the end of a pasteur pipet. The final product should be massed and stored in a tightly capped vial for subsequent GC analysis.
Your instructor has written data acquisition programs for the esters in this experiment so that no additional instrument set-up is required on your part. The detector for the GC is the HP 5790 Mass Spectrometer. As each substance emerges from the column it is not only quantified but also analyzed and the mass spectrum for the substance (which is stored with the data output) can be subsequently compared with a library of standard spectra for identification. You will be furnished with a computer-generated report on your sample on the day following injection. Everyone will use the same acquisition routine but you must be sure to enter a unique file name for your data since it will be processed after class hours. Follow the instructions below carefully.

1. Press F2 to begin **Data Acquisition**.
2. Press F5 to **Load Parameters**. Type in place of the parameter file shown:
   \[ \text{PARAM:ESTER.A} \]
3. Press F5 again to **Load** the actual parameter file. This is very important. If you simply press <Return> instead, the parameter file will not be loaded.
4. Press F1 to **Prepare to Inject**.
5. Type in the data file space:
   \[ \text{DATA:1.D} \] (substitute your locker number for the 1)
   Follow by <Return>. Please do not use any other kind of file names. These are the only kinds of files the instructor will look for when processing the data.
6. Use TAB to move to the operator name field and type in your name.
7. Wait for temperature equilibration and the message **Ready to Inject**.
8. Use the "empty syringe" method to inject your mixture and start the run. Wait for run completion.
9. Press F8 (Exit, Quit) twice. This should leave the instrument as you found it, ready for the next student.

The calorimetry measurements are done while students are taking turns injecting their simple esters into the GC during the second day of the experiment. For each trial use 100 mL of pre-chilled water and heat with whichever fuel until the temperature of the water rises by about 20 degrees. Because the biodiesel and petroleum diesel are not very volatile, slightly more exposed wick is needed to sustain a flame than for the octane. These two fuels are also absorbed more slowly by the wick so it might be wise to fill the burners right away and let them sit while you work with the octane. If you are having trouble lighting any of the fuels, ask the instructor for help. Mass the fuel burner both before and after to determine how much fuel was burned.

Be sure to check the bottom of the can between trials and note the amount of soot produced. The collection of soot indicates incomplete combustion and therefore a less efficient fuel (at least under the conditions of this experiment). Clean off the soot between trials. At the end of the experiment, clean off any adhering soot and place the can in the oven to help prevent rusting.
The Report

Your initial calculations should include:

1. The theoretical yield from the esterification based on the masses of the acid and alcohol
2. The "actual" yield as determined from the mass of the collected and dried product
3. The probable identity of components in your mixture based on Mass Spectra library database match
4. The calorimeter constant [the heat of combustion for octane is -5450 kJ/mol]
5. The heat per gram released by the burning of biodiesel and petroleum diesel

Your conclusion to the first part of the experiment should include a reaction for the production of your simple ester. Use structural formulas. Give the correct name of the ester and its handbook boiling point along with a 3D molecular diagram.

Why would concentrated hydrochloric acid NOT be a good choice for a catalyst in the esterification reaction? [hint: how much water is present in each concentrated acid?]

Your conclusion to the biodiesel portion of the experiment should include a brief comparison of the per-gram energy yields of the three fuels. Do the fuels burn equally clean under the conditions of this experiment?

Take a look at the IR and NMR spectra for the original olive oil, the biodiesel, the glycerol by-product, and the petroleum diesel fuel and address the remaining questions. (all spectra provided at the end of this experiment).

The fatty acid that makes up olive oil is largely (about 80%) oleic acid (C_{18}H_{24}O_{2}):

\[ \text{Remember, three of these acid molecules react with glycerol to form a triple ester that is olive oil (the bulk of this molecule is the "R" group on the triglyceride structure shown earlier). Oleic acid is mono-unsaturated. Based on the structure above, is the molecule \textit{cis}- or \textit{trans}-? Locate evidence for this structural element (C=C) in the NMR spectrum for olive oil. Is there also evidence for this feature on the IR spectrum for olive oil? Can you tell from the IR if the molecule is \textit{cis}- or \textit{trans}-? There is a very large peak in the NMR for olive oil at } \delta = 1.3. \text{ Based on the molecular structure above and the correlation tables in your lab text, what structural element in the molecule probably accounts for this peak?} \]
In the IR spectrum for olive oil locate and identify a peak which reveals a characteristic structural element present in the ester. Is this peak also present in the biodiesel IR spectrum? Explain.

In the NMR spectrum for the biodiesel there is a singlet at $\delta = 3.6$ which is not in the spectrum for olive oil. Based on your understanding of the reaction and the correlation tables, what is the likely source for this peak? Does the double bond from the oleic acid persist in the biodiesel? Explain with reference to the NMR and the IR spectra.

The structure of glycerol, $\text{C}_3\text{H}_8\text{O}_3$, is shown below.

What feature of the IR spectrum for the lower layer of the vial contents appears to confirm that the this part of the reaction mixture could actually be glycerol?

The NMR and IR spectra for petroleum diesel are fairly simple. Compare on-line spectra for octane, nonane or decane and comment on the likely contents of the petroleum diesel (which is a mixture).
IR for olive oil

NMR for biodiesel derived from olive oil
IR for biodiesel derived from olive oil

IR for lower layer by-product
NMR for petroleum diesel

IR for petroleum diesel