

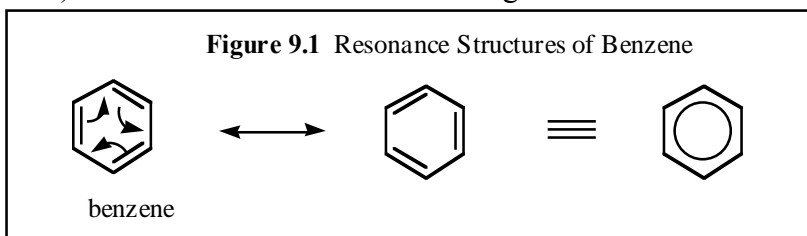
Experiment 9

Qualitative Tests For Hydrocarbons; Unknown Hydrocarbon

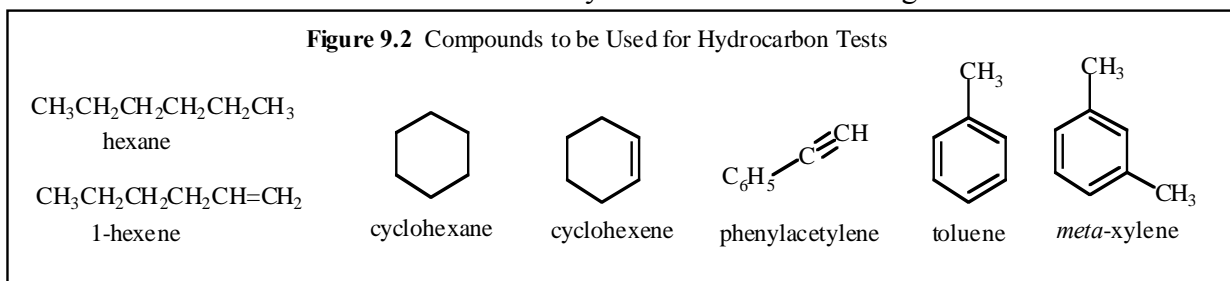
Hydrocarbons can be grouped into four structural classes and simple chemical tests can be used to distinguish between these classes. In this experiment you will perform five such qualitative analytical tests, first using known hydrocarbons, and then you will perform the same tests on an unknown hydrocarbon so as to determine its chemical class.

The four classes of hydrocarbons are as follows:

- (1) Alkanes – These are saturated hydrocarbons with only single bonds.
- (2) Alkenes – These are hydrocarbons that contain at least one carbon-carbon double bond.
- (3) Alkynes – These are hydrocarbons that contain triply bonded carbons.
- (4) Aromatics – These are hydrocarbons that contain an aromatic ring. An aromatic ring is a circular arrangement of alternating double and single bonds that is particularly stable due to the delocalization of electrons around the ring. Though the aromatic compound appears to have double bonds, these double bonds do not behave in the expected manner. They are much less reactive than normal double bonds. This is due to the fact that they are not really double bonds but a mixture of double and single bonds (or a one and one-half bond). This can be seen in the following resonance structures for benzene.



For the first three tests we will use the hydrocarbons shown in Figure 9.2.



Test 1: Sulfuric Acid Solubility Test

The π -electrons of alkenes and alkynes are very reactive toward sulfuric acid (and other sources of H^+). The π -electrons attack the H^+ to form a carbocation, which either reacts with the bisulfate anion or react with the π -system of another alkene (Figure 9.3). Alkynes react similarly. Alkanes and aromatics do not produce any visible reaction with concentrated sulfuric acid under these conditions.

Procedure:

Set-up 7 small, dry test tubes. Add about 1.5 mL **COLD** concentrated sulfuric acid to each test tube. Add 3-4 drops of hexane. Stir with a clean stirring rod. Record your observations in your notebook. Look for some evidence that a reaction has occurred. This evidence may include changes in color, temperature, the formation of one layer or two layers. Repeat with the other test hydrocarbons. **CAUTION: alkynes react very vigorously with the sulfuric acid!! Add only 1-2 drops of the alkyne. The reaction can be exothermic and cause splattering. Point the test tube away from your eyes and your neighbor and hold the test tube with the wire test tube holder.**

Figure 9.3 Reaction of sulfuric Acid with Alkenes

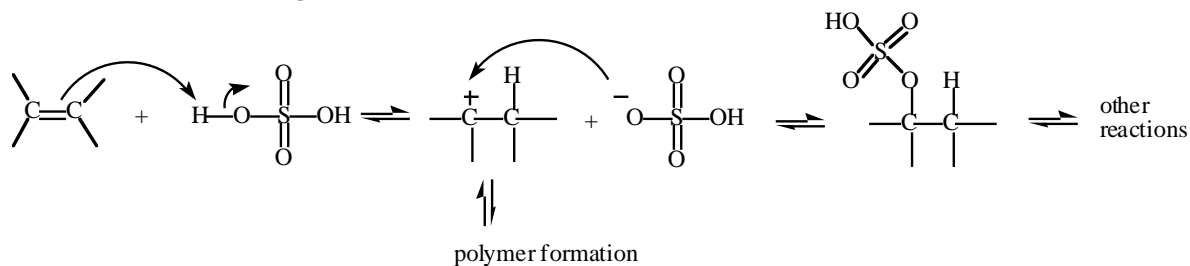
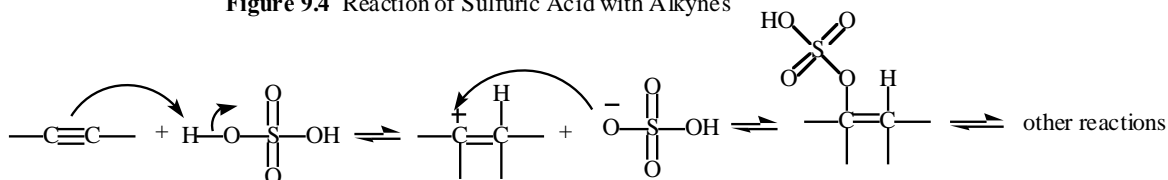


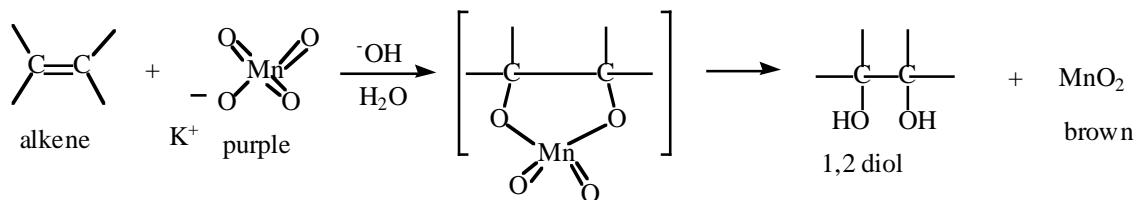
Figure 9.4 Reaction of Sulfuric Acid with Alkynes



Test 2: Baeyer Test (Potassium Permanganate Oxidation)

Potassium permanganate (KMnO_4) will react with alkenes and alkynes to form 1,2-diols. As the alkene or alkyne is oxidized, the purple color of permanganate disappears and is replaced with the brown color of the reduced MnO_2 . This reaction is shown below with alkenes.

Figure 9.5 Permanganate Oxidation of Alkenes



Procedure:

To each of 7 small test tubes (they do not need to be dry) add 2 mL H_2O and 3-4 drops of each of the seven test hydrocarbons listed above.

Add one drop of purple 2% KMnO_4 solution and shake vigorously, using a small cork to stopper the end of the test tube. Record your observations for each hydrocarbon tested.

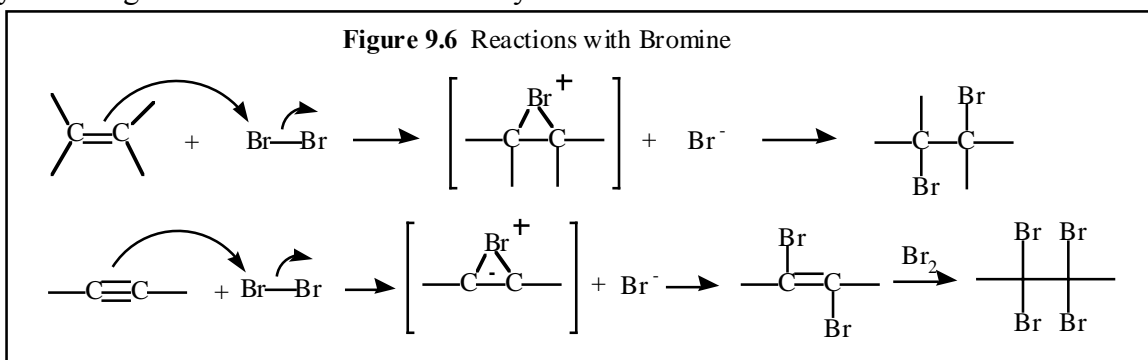
Test 3 Bromine in Carbon Tetrachloride

Bromine is an excellent electrophile and will react with the nucleophilic π -electrons of both alkenes and alkynes to form a bromonium ion, which then reacts with Br^- to give a dibromo addition product as shown in Figure 9.6.

Procedure:

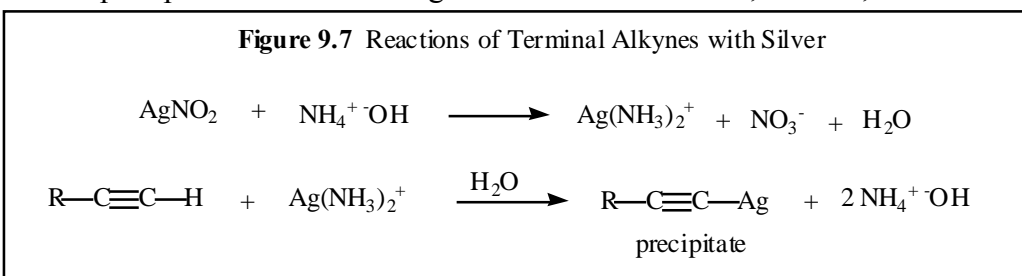
Set up 7 small, dry test tubes and add about 1 mL (20 drops) carbon tetrachloride to each test tube. Add 3-4 drops of test hydrocarbon to each test tube as in Test 1 and Test 2. Add 2-3 drops of 5% bromine in carbon

tetrachloride and record your observations. Repeat for all of the 7 hydrocarbons being tested. Continue the drop-wise addition of bromine until its red color persists. Record the number of drops in each case. You will notice that alkynes consume twice as much bromine as alkenes to give a tetrabrominated adduct. This will help you distinguish between alkenes and alkynes



Test 4: Silver Nitrate Test

This test is different from the first three in that it is specific for terminal alkynes and distinguishes them from alkenes and non-terminal alkynes. You will do the test on two different hydrocarbons (an alkene and a terminal alkyne). First, you make your test reagent by mixing a solution of silver nitrate with ammonium hydroxide. Under these conditions, Ag^+ replaces the acidic hydrogen of a terminal alkyne to form a light colored precipitate as shown in Figure 9.7 below. Alkanes, alkenes, and aromatics do not react with $\text{Ag}(\text{NH}_3)_2^+$.



Procedure:

First you will make your test solution. Add 2 mL of 5% silver nitrate to a small test tube. Add 2 mL concentrated ammonium hydroxide solution, NH_4OH . This should be done in the hood. Ammonium hydroxide has a **BAD SMELL** due to ammonia escaping but is relatively odorless once it has been mixed with the silver nitrate.

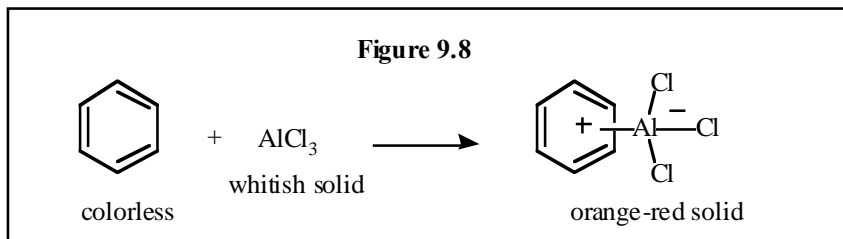
Add 1 mL of the test solution to each of 2 small test tubes. To the first test tube, add three drops of a terminal alkyne. Stir and look for the formation of a white precipitate.

Repeat using hexene.

Test 5: Test for Aromatics (Friedel-Crafts Test)

Strong Lewis acids such as aluminum trichloride will react with the relatively unreactive π -electrons of an aromatic system to form a bright orange-red colored complex (Figure 9.8). It will also react with alkenes and alkynes to form a colored complex, though the color will be different from the color generated with an aromatic system. (Usually it is more yellowish with double and triple bonds).

This test is good for discriminating between alkanes and aromatics, both of which give negative results with the other four tests used so far. Do this test with an alkane and an aromatic compound.

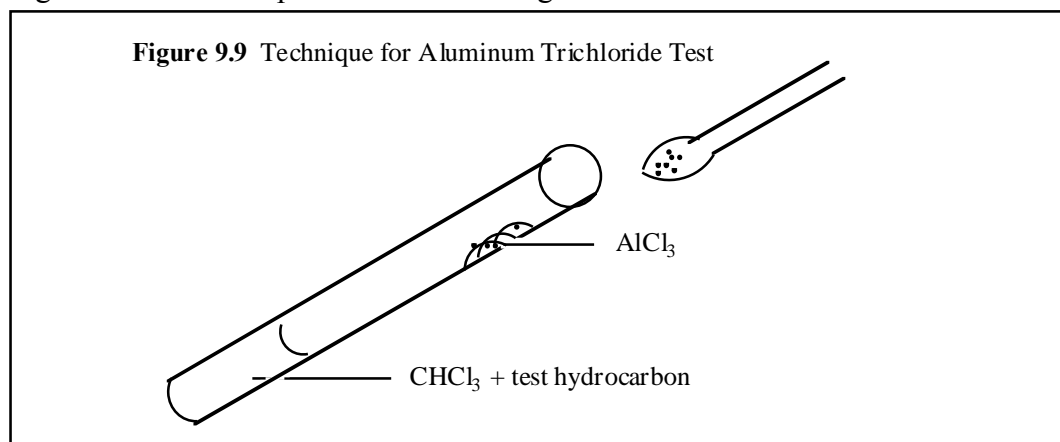


Procedure:

Prepare a small, dry test tube. It must be thoroughly dry since AlCl_3 reacts with water. Add 2 mL chloroform (CHCl_3) and 3-4 drops of your test compound. Then add a spatula tip of AlCl_3 to the upper inside part of the test tube (tilt the test tube in order to do this).

Note: Aluminum chloride is very hygroscopic (reactive toward water). You must close the AlCl_3 bottle tightly immediately after use; otherwise the contents become deactivated by reaction with water vapor in the air.

Now tilt the test tube some more so that the solvent wets the solid material as shown below. You should see a rapid color change in the solid. It should turn bright orange-red with a compound containing an aromatic ring. Alkanes do not produce such a change.



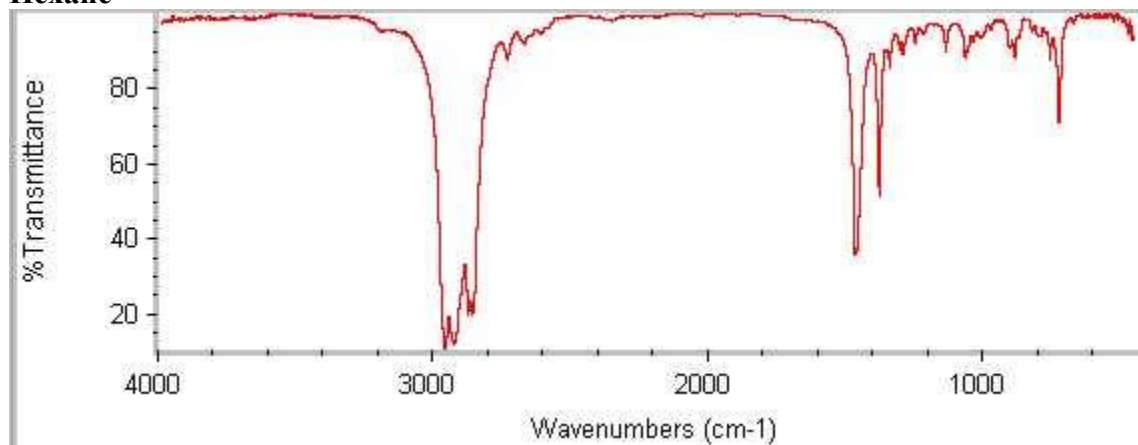
Unknown Hydrocarbon

When you have finished all of the tests with the known hydrocarbons and you are confident that you can distinguish between a positive and negative test for each type of hydrocarbon, get an unknown hydrocarbon from the teaching assistant. Record the unknown number in your notebook and then devise a strategy to identify whether it is an alkane, alkene, terminal alkyne or aromatic on the basis of the tests above. Record all results in your notebook. On the basis of the tests you should be able to determine which class of hydrocarbon your unknown is in (alkane, alkene, alkyne, terminal alkyne, aromatic).

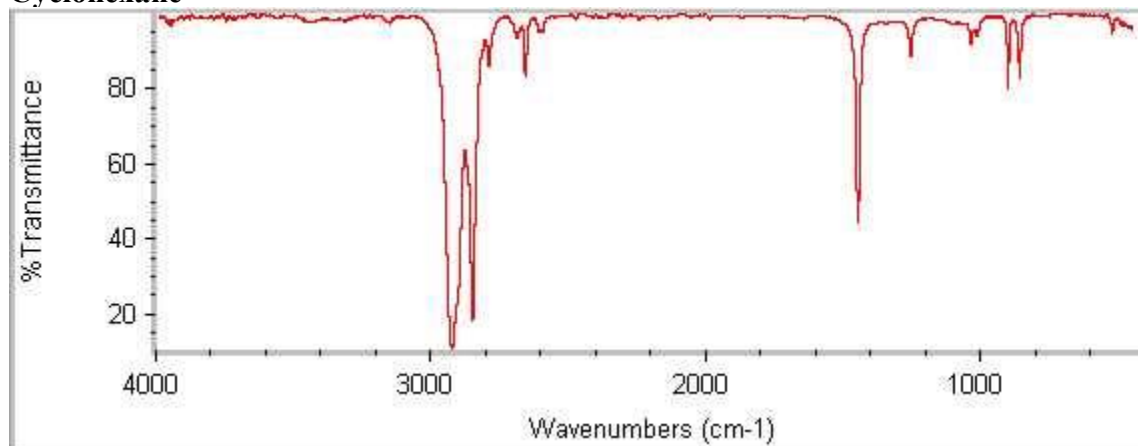
Then obtain an IR spectrum of your unknown and you will make a positive identification by comparing it to the IR spectra given in appendix 9.1.

When you have finished, turn in your Unknown Report Sheet, listing the results of the chemical tests you performed and giving your overall conclusion.

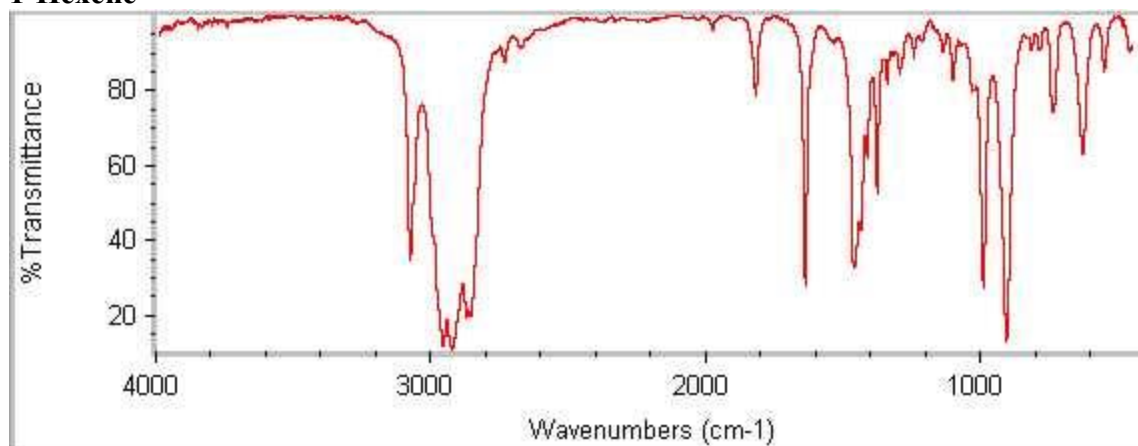
Appendix 9.1 Infrared Spectra of Hydrocarbon Unknown Hexane



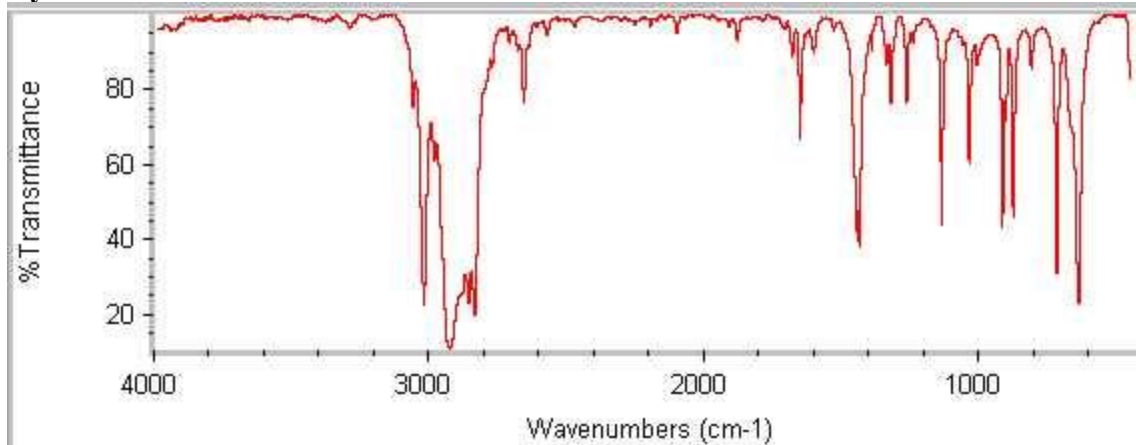
Cyclohexane



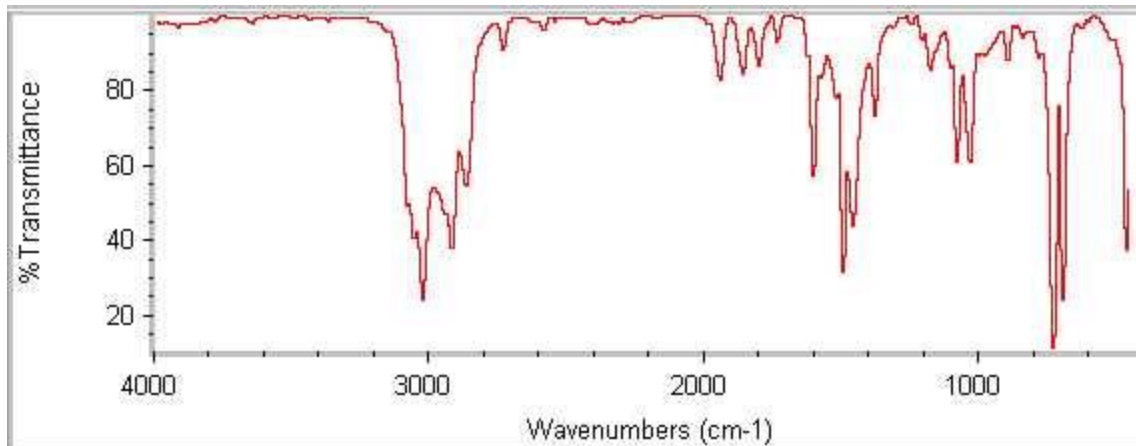
1-Hexene



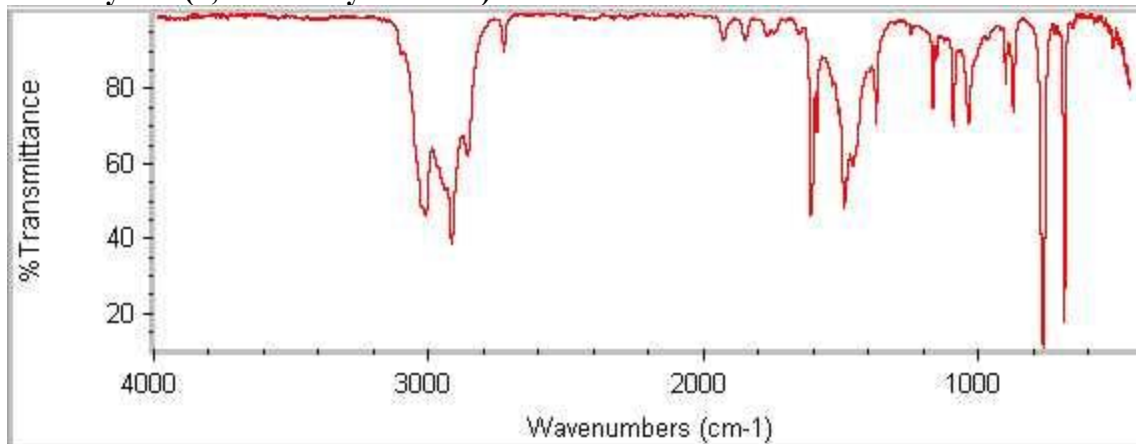
Cyclohexene



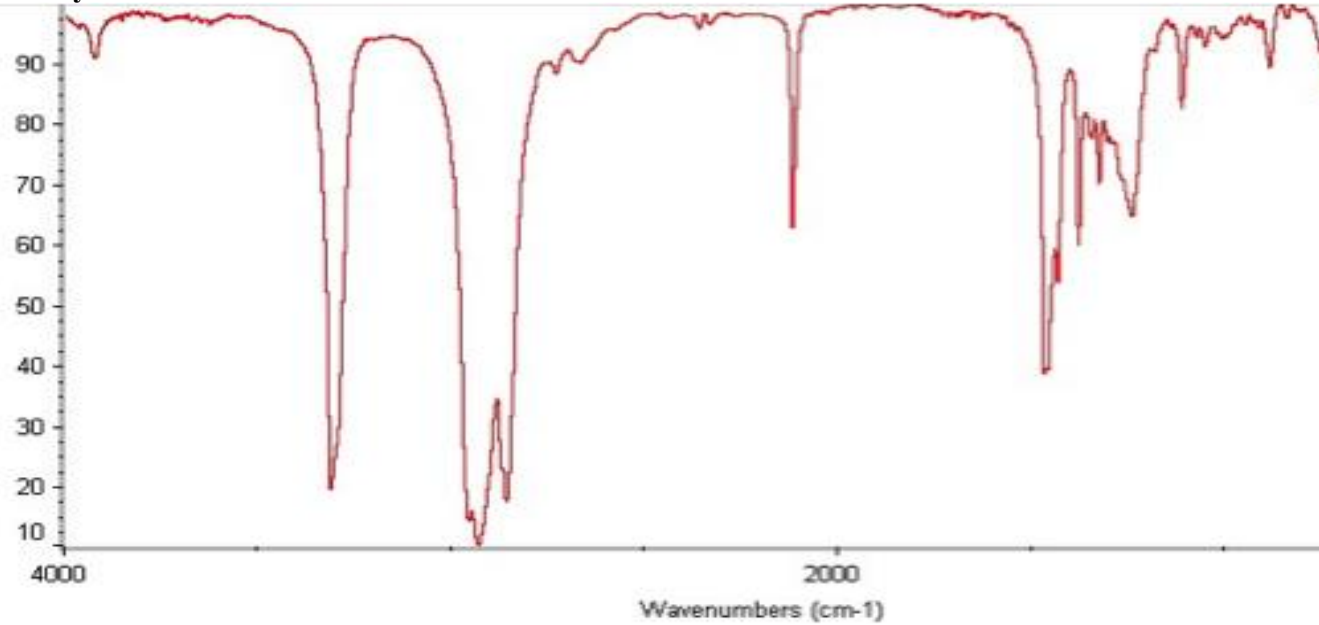
Toluene



meta-Xylene (1,3-Dimethylbenzene)



1-Octyne



Phenylacetylene (phenylethyne)

