Analysis of products by infrared spectroscope and tlc essay sample

The objective of this lab experiment was to isolate (S)-(+)-Carvone from Caraway Seeds and (R)-(-)-Carvone from spearmint leaves through process of steam distillation by extracting the distillate with CH_2Cl_2. In addition, infrared spectroscopy, Bayer test, and thin-layer chromatography was performed to analyze the distillate samples. By performing such methods, the enantiomers of the carvone were examined.

In the liquid phase, the molecules are constantly in motion. Some molecules at the top of the surface escape to the vapor phase. A closed system is in dynamic equilibrium when the number of gas molecules exiting the liquid phase is equal to the number of gas molecules entering the liquid phase. The vapor pressure of a liquid is the pressure that the gas molecules exert against the walls when they collide.

Vapor pressure increases as temperature increases because the molecules have more kinetic energy. More molecules escape to the gas phase. The boiling point is where the vapor pressure equals the total atmospheric pressure. Therefore, the higher the vapor pressure, the more molecules are in the gas phase. The boiling point would be lower since more gas molecules escape faster at a lower temperature. Evaporation occurs faster as more gas molecules escape faster. Dalton's law is $P_{total} = P_{sample} + P_{air}$. It can be used to calculate the pressure of a system when the system is not closed and air is included.

The vapor pressure of a system can change as volatile and nonvolatile impurities are added. The presence of a nonvolatile impurity decreases the vapor pressure at any temperature by a constant amount. Raoult's law determines the relationship between vapor pressure and the composition of homogeneous liquid mixture. It states that the partial pressure of component X is equal to the vapor pressure, Pox, times the mole fraction, Nx: Px = PËxNx. The mole fraction can be determined by dividing the number of moles of X by the sum of the number of moles of all components: Nx= (nX)/(nX + nY + nZ + …). When there are two or more volatile components then the total vapor pressure is equal to the sum of the partial vapor pressures: Ptotal = Px + Py + Pz +… otherwise known as Dalton’s law only it includes more than one component.

Enantiomers are compounds that have the same molecular formula and structure, but they differ in the placement of molecules around an asymmetrical carbon atom called a stereocenter. The stereocenter has four different groups attached to it and can either be rectus (R or clockwise) or sinister (S or counter-clockwise) configuration. The configuration is determined by the Cahn-Ingold-Prelog rules. This difference in configuration causes the molecules to be non-superimposable or mirror images of each other.

The molecules can also cause light to rotate in different directions. If the enantiomer rotates the light clockwise, then it is dextrorotatory or positive and if it is counter-clockwise, then it is laevorotatory or negative. The polarimetry and the stereocenter configuration direction are independent of each other. Plane polarized light must be used to determine whether it is positive or negative and this is different for each different pair of enantiomers. For example, for one set of enantiomers could have R+ and S- while another set could be R- and S+. This is the case for carvone in this lab.

Carvone is (S)-(+)-carvone and (R)-(-)-carvone. The two sets of enantiomers are shown below:

(R)-(-)-Carvone (S)-(+)-carvone

Spearmint Leaves Caraway Seeds

Figure 1: Enantiomers of (R)-(-)-Carvone and (S)-(+)-carvone

The only difference between the S and R configurations of carvone are their stereocenter. The S form is found in caraway seeds and the R form is found in spearmint leaves. Since these two compounds have the same boiling point, melting point, densities, color, viscosity, infrared spectra, indices of refraction, and thin layer and gas chromatography, the only way to differentiate them is by their polarimetry and scent. Their polarimetry is determined by using plane polarized light. Most people can smell the differences but others cannot. The nose contains hundreds to thousands of receptors on the olfactory neurons that can identify different molecules. Therefore, the reason that the nose can tell the difference between enantiomers is that it is chiral.

Carvone are monoterpenes, meaning that they have ten carbons and two isoprenes. The (R)-(-)-Carvone smells like spearmint and is major component of spearmint oil which also contains minor amount of limonene (strong smell in oranges; used in chemical synthesis as a precursor to carvone). Comparatively, (S)-(+)-carvone is found in caraway seeds and also contains limonene. The (S)-(+)-carvone is mainly responsible for the characteristic odor of these oils. Both of these enantiomers do not occur naturally nor are they readily available from readily accessible source. There, via distillation process they can be isolated and be commercially available.

Distillation is laboratory technique used for separating and purifying liquids. It is powerful tool, both for the identification and the purification of organic compounds. Simple Distillation and fractional distillation are often used for isolation of mixture of liquids; however with simple distillation volatile organic compounds that are immiscible or insoluble in water such as oil can be separated. Therefore, in this experiment, steam distillation is used to separate carvone from caraway seeds and spearmint leaves.

For steam distillation, distill liquids boiling point has to be less than 100° C, compound mixed with water has to be stable at 100° C and its vapor pressure should be greater than 5 Torr at 100° C. In this process, volatile liquids and oils co distill with water. The principles of steam distillation focus on Raoult’s law and Dalton’s law. According to Raoult’s law partial pressure of compound equals mole fraction of that compound multiply by vapor pressure. If Raoult’s law is applied for immiscible component (X) in a heterogeneous mixture with water, then partial pressure of X equals vapor pressure of X.

Since X is not soluble in water, it does not depend on its mole fraction in the mixture. Therefore, Raoult’s law does not apply to steam distillation because the compounds are immiscible, so they do not depend on each other’s mole fraction. According to Dalton’s law, total vapor pressure equals sum of individual vapor pressures. So, total vapor pressure is higher than most volatile component and boiling point mixture is lower than the lowest boiling component due to the higher total vapor pressure. Normally, distillation process of these liquids would require high temperature; however, with presence of water other components of mixture boil below its normal boiling point.

Steam distillation apparatus requires same glassware similar to other distillation methods such as still pot flask, a condenser tube, a thermometer adapter, and a separatory funnel as well. Separatory funnel is important because in steam distillation, water must be continuously added to the stillpot. This is because the water is being vaporized along with the sample, so water is added at the rate that is distills out so the volume stays nearly constant. The process begins by placing the sample in still pot with hot water. As the sample is boiling, it vaporizes and passes through the condenser tube. The sample gets condensed along with water vapor and then collected as distillate. Then, as the distillate is received the separatory funnel is opened to allow water to drip in the still pot. After obtaining the distillate, it is extracted with methylene chloride. Once it is extracted, it will then be separated from the water by using a chemical that is miscible; in this experiment, it is Na2SO4.

Figure 2: Steam Distillation Apparatus

After the process of steam distillation, Thin-layer Chromatography can be applied as an analytical tool for rapid analysis of small quantities of samples. Thin layer chromatography (TLC) is like column chromatography except that the stationary phase is bound to a layer of silica. Tiny spots of the different molecules are placed on a baseline. The solvent is then added and it travels up the piece of plate. The folded piece of filter paper can be used for solvent equilibrium. The molecules attach to the solvent, which serves as mobile phase. The farther the compounds move, the more non-polar they are because they have a higher retention factor.

When the solvent stops moving up the solid, so do the molecules. They leave a visible mark where they stopped moving. The retention factor (Rf) can be measured with the following formula: Rf = (distance traveled by the substance) / (distance traveled by the solvent). The higher the retention factor is then the lower the retention time. Therefore, if the solvent is in the mobile phase longer, then it will have a higher retention factor. Besides determining which substances are more polar, TLC can also be used to determine is two compounds are different.

Figure 3: Thin-Layer Chromatography Chamber

Lastly, Infrared spectrometry is used to verify the separation. Infrared spectrometry can determine the different types of functional groups in a molecule. When increasing energy is sent through the molecule, radiation is absorbed by different functional groups and this corresponds to different transitions among vibrational-rotational levels. The bonds between the atoms vibrate at a frequency that is read by the IR spectrometer. As this frequency increases, so does the wave number of the groups and radiation energy. Hooke's law can be used to calculate the stretching frequency of the bonds: Î°= √(k)/(2πc√(m*)) where c= speed of light, k= force constant of bond, and m*= reduced mass of atoms joined by bond (mAmB)/(mA + mB).

Different functional groups exhibit different frequencies and intensities. Alkenes have a frequency around 1600-1660cm-1 with variable intensities. Carbonyl groups have a variety of different frequencies and intensities depending on the other groups in the molecule or where the carbonyl group is. Ketone has a frequency of around 1705-1725cm-1 with strong intensity. However, because carvone has a ketone attached to six membered ring with a double bond, the frequency is lowered. Therefore, the frequency for carbonyl group in carvone is about 1675cm-1. Since (S)-(+)-Carvone and (R)-(-)-Carvone are enantiomers, IR spectra for both enantiomers of carvone are identical. The Rf value of a compound is a physical constant for a given set of chromatographic conditions.

By performing these various methods, (S)-(+)-Carvone from caraway seeds and (R)-(-)-Carvone from spearmint leaves were isolated. It was determined that the enantiomers have the same boiling point, IR spectrum, and retention factor. However, each enantiomer has unique smell and they differ in their optical rotation direction.