Name
CHE 173 Sec #
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Experiment 36: Determination of the Structure of a Natural Product in Anise Oil

Purpose: The purpose of this experiment is to isolate the major component of anise oil and determine its identity and structure using melting point determination and IR spectroscopy.

Introduction: The major component of anise oil has the chemical formula $C_{10}H_{12}O$. This compound is said to be hydrogen deficient, meaning that it contains less hydrogen atoms than would be needed for each of the carbon atoms to have the maximum amount of hydrogen atoms attached. The IHD, or index of hydrogen deficiency for this molecule is 10. This indicates that there must be five rings or double bonds in the structure. Each of these would compensate for two of the missing hydrogen atoms. Since a saturated compound of the chemical formula $C_{10}H_{20}O$ is formed upon catalytic hydrogenation of anise oil, it can be determined that the original structure contains four pi bonds, as eight hydrogen atoms were added. Through heating with hydriodic acid, anisene forms the phenol C_9H_9OH. This indicates that the major constituent of anise oil is an aryl methyl ether, with the chemical formula $C_9H_9OCH_3$. With the formula rewritten, it can be seen that anisene has a disubstituted benzene ring with a methoxyl group ($-CH_3O$). This means that the remaining constituent is $–C_3H_5$. In this experiment, anisene can then react with a methoxybenzoic acid to yield one of three products. The identity of the product, which can be decided by a melting point and IR spectrum analysis, can then infer the position of

the second substituent, and the overall structure of the major component of anise oil can be discovered (Lehman 292-294).

Materials and Methods: The materials and methods used during this experiment may be found in the laboratory manual (Lehman, p. 295-296). However some changes to the experiment procedure were made. Instead of five minutes, which was stated in the laboratory manual, the original reaction mixture, consisting of water, potassium permanganate, and tricaprylmethylammonium was placed in the boiling water bath for 10 minutes to ensure a complete reaction. After adding the anise oil, the mixture was allowed to heat for 20 minutes rather than 15 minutes as stated. Lastly, the IR spectrum analysis was previously prepared so no actual IR spectrum analysis was carried out during the course of the experiment.

Results: No substantial qualitative data was collected, except that the original reaction mixture turned a purple color. Upon the addition of anise oil and heat, the reaction mixture turned a brown color. And with the addition of $NaHSO_3$ the mixture turned a white color. The mass of the final product sample was measured to be 0.08g (see Calculation 1). The melting point range for this sample was 172.8-185.4ºC in Trial 1 and 171.6-185.2ºC in Trial 2 (see Table 1). The IR spectrum of anise oil can be found attached. Peaks appear to exist at 3022.86, 3002.41, 2957.58, 2933.88, 2912.63, 2834.94, and 2723.19 (cm^{-1}). Another set of peaks appear to exist at 1608.06, 1510.55, 1464.73, 1441.16, 1306.3, 1283.06, 1247.18, 1174.78, 1036.26, 964.58, 839.29, and 787.03 (cm^{-1}). No other significant quantitative results were collected.

Discussion: As seen in the melting point determination, the average melting point range of the product was 172.2-185.3ºC. The melting points of the possible products are listed as 101ºC for *o*-methoxybenzoic acid, 110ºC for *m*- methoxybenzoic acid, and 185ºC for *p*- methoxybenzoic acid. As the melting point of the sample was 185.3 ºC, this data resembles the melting point of *p*- methoxybenzoic acid most closely. Therefore, since the melting points of the other possible products are rather distant from the experimental value, it can be determined that the structure is most likely *p*- methoxybenzoic. This, of course, is assuming that major experimental error did not occur. Since the melting point was slightly higher than the expected value however, it could be determined that some error most likely occurred. For example, the exact starting and ending melting points could have been misjudged. Further error could be found in the final mass of the product. Even though a small yield was expected, it could be seen that some sample was lost in transferring the mixture to different containers. The final mass of the product should have no substantial effect on the melting point analysis. Even with the identity of the product found to most likely be *p*- methoxybenzoic, the IR spectrum analysis is still necessary. A complete analysis of the IR spectrum can be seen in Table 2, with each peak and its possible corresponding structures. However, as the formula of the structure is already known, only the placement of the second component is needed. Therefore, only the part of the spectrum which considers the placement of the substituents may be analyzed. *Ortho* substitution has a frequency range of 735-770 (cm^{-1}). *Meta* substitution has a frequency range of 750-810 and 680-730(cm^{-1}). *Para* substitution has a frequency range

of 790-840(cm^{-1}). The peaks found on the IR spectrum in these ranges were 787.03 and 839.29 (cm^{-1}). From this it can be determined that the product does not have *ortho* (1,2) disubstitution. Also, as only one of the two given peaks resides in the range for *meta* (1,3) disubstitution, it can be inferred that the rings does not contain this type of substitution. Although the peak at 787.03 cm^{-1} falls slightly out of the range of *para*-disubstitution (1, 4), it is fairly close to the 790 cm^{-1} lower limit. The second peak at 839.29 cm^{-1} falls well within this given range. Therefore, it can be determined that the structure most likely contains *para*-disubstitution. This, along with the melting point data, suggests that the product of the reaction was *p*-methoxybenzoic acid. This structure may be seen below:

References / Literature Cited:

Carey, Francis A. *Organic Chemistry*; McGraw Hill, New York, NY, 2003, Table 13.4 Infrared Absorption Frequencies of Some Common Structural Units, p.561.

Lehman, John; *Multiscale Operational Organic Chemistry*; John Challice, Prentice Hall, New Jersey, 2002, Experiment 36: Determination of the Structure of a Natural Product in Anise Oil, p.291-297.

Figures, Tables, Data, Spectra:

Calculation 1:

The mass of the final product can be found using the calculation below:

$Mass_{evaporating\ dish\ +\ sample}$ - $Mass_{evaporating\ dish}$ = $Mass_{sample}$

72.32g – 72.24g = 0.08g

The melting point data collected for the anise oil component can be found below in Table 1:

Table 1. Melting point ranges for product sample according to T (ºC) at the beginning of melting and completion of melting

Trial	Beginning of melting (ºC)	Completion of melting (ºC)
1	172.8	185.4
2	171.6	185.2
Avg	172.2	185.3

The peaks found on the IR spectrum of anise oil and the corresponding structure related to each peak can be found in Table 2 below:

Table 2. Peaks from IR spectrum data and possible corresponding structures.

Peak (cm^{-1})	Corresponding structure
3022.86	sp^2 C-H
3002.41	sp^2 C-H
2957.58	-OH
2933.88	sp^3 C-H
2912.63	sp^3 C-H
2834.94	-OH
2723.19	-
1608.06	-
1510.55	-
1464.73	-
1441.16	-
1306.03	-
1283.06	-

1247.18	-
1174.78	sp^3 C-O
1036.26	sp^3 C-O
964.58	RCH=CHR (trans)
839.29	Para-substituted
787.03	Para-substituted