

Esterification of Artificial Flavors. Synthesis of Isoamyl Acetate.

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Abstract:- The present research work aimed to study the synthesis of isoamyl acetate from isoamyl alcohol, using the Fischer esterification method that was based on the formation of an ester by refluxing a carboxylic acid and an alcohol, for this purpose. 5.3 mL of isoamyl alcohol and 7.3 mL acetic acid were used, which were mixed in a round bottom flask and then 1.2 mL of sulfuric acid was added while the flask was shaken, in addition these tests allowed to identify that They are highly exothermic reactions due to the evolution of heat. The reflux condenser was then coupled with lightly greased tips and boiled on the hot plate, keeping the reflux for a time of one hour. At the end of this time, it was allowed to cool to room temperature and all the liquid was transferred to a separatory funnel with 10 mL of ice water. It was gently stirred, and decanted separating the lower aqueous layer. Subsequently the resulting organic layer was washed with sodium bicarbonate, to remove excess acetic acid. In this extraction process, there was release of CO₂, which caused an overpressure inside the funnel. Subsequently, the extract was verified with pH indicator paper to determine the basicity of the organic layer with pH 8. Subsequently, the organic phase was dried with anhydrous sodium sulfate followed by a decantation and a distillation that allowed us to obtain a colorless liquid with a strong characteristic smell of banana. Finally, the amount of isoamyl acetate obtained in the reaction was determined, which was 4.2 mL and the reaction yield calculations were made, which gave a percentage of 58.09%, which is very acceptable.

Keywords:- Esterification, Artificial Flavors, Isoamyl Acetate.

I. INTRODUCTION

Artificial flavors known as esters are highly attractive not only at an academic level but also at an industrial level, since they make up the group of compounds that significantly affect the sensory quality of the final product. The production of this type of compound has traditionally been achieved by chemical synthesis, from the extraction of the plant (Romero, Calvo, Alba, Daneshfar, & Ghaziaskar, 2005).

Ester formation originates during primary fermentation and is highly associated with lipid metabolism and yeast growth. These compounds are synthesized in the cytoplasm from reactions catalyzed by enzymes and if they occur in the absence of oxygen there are reactions such as acetyl-CoA that in the presence of alcohol (ethanol or higher alcohols) allow the formation of acetate esters, such as ethyl acetate, isoamyl acetate, isobutyl acetate and phenylethyl acetate that are of great importance for final products with aromatic profiles (Loviso & Libkind, 2018). Today isoamyl acetate is one of the most widely used in the food industry around 74,000 kg / year for its characteristic banana flavor (Romero et al., 2005).

Acetic acid reacts with isoamyl alcohol to give the isoamyl acetate ester and to improve the conditions the presence of a cation exchange resin catalyst is recommended, which can be styrene divinylbenzene sulfonated (CT-175) (Teo & Saha, 2004) or presence only of sulfuric acid. The conversion of carboxylic acid with alcohol and its transformation into an ester is known as "Fischer's esterification" (Corregidor, Acosta, Gonzo, & Destéfanis, 2018). The Fischer-Speier esterification or Fischer esterification is a special example of esterification, since it is a special type of reaction that is based on the formation of an ester by refluxing a carboxylic acid and an alcohol as shown in Figure 1.1, based on the electrophilicity of carbonyl carbon that is activated in the presence of an acid catalyst. All carboxylic acids are capable of generating this type of reaction, but the alcohol must be a primary or secondary alcohol because tertiary alcohols are susceptible to elimination, and phenols tend to be very little reactive to give advantageous yields (Camacho & Márquez, 2013).

The reaction mechanism for the synthesis of isoamyl acetate has several steps; As a first step, there is a protonation of the oxygen of the carbonyl group, and it activates it against a nucleophilic attack of the isoamyl alcohol, this causes the loss of the hydrogen proton and gives rise to the hydrate of an ester. Subsequently, the loss of water from the hydrate of an ester occurs. The protonation of one of the two hydroxyl groups of the hydrate makes it a good leaving group, water. After the process where the release of water occurs, a cation stabilized by resonance is formed. The loss of a proton (originating from the second hydroxyl group) gives rise to the ester (Wade, 2004). Figure 1.1 shows the reaction mechanism for the synthesis of isoamyl acetate.

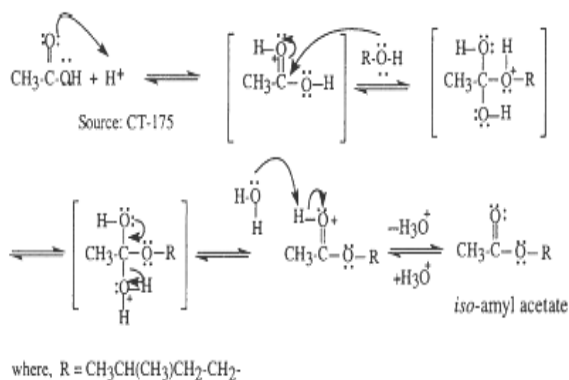


Figure 1.1. Reaction mechanism

In chemical reactions that use distillation methods, where the conversion to the products of interest is limited by the importance of the chemical equilibrium, the selective removal of the products is a way to increase the production efficiency as mentioned by the Le Chatelier principle; This can be done based on the property that substances have to distribute unevenly in the vapor-liquid phases, present within the unit distillation operation (Leiva et al., 2004).

II. EQUIPMENT AND MATERIALS

A. Equipment

Balance

Stirring heating plate

B. Materials

- 250 mL Kitasato flask
- Universal support
- Clamp for universal holder
- Latex hoses
- For film
- Glass Pasteur pipettes, long and short tips
- Suction rubbers, dropper type
- 10ml, 20ml and 50ml cylinders
- Suction pear
- Spatula
- Thermometer
- Monohorada and bihoradado plugs of various diameters
- Test tubes
- Cigarette lighter
- PH paper
- Lighters
- Gas cylinder
- Separation funnels
- 50 ml and 100 ml
- 10 and 20 ml flat bottom bottles with 14/10 and 29/32 joints

C. Reagents

- Isoamyl Alcohol
- Glacial acetic acid
- Concentrated sulfuric acid
- Emery grease
- 10% sodium bicarbonate

- Sodium chloride 25%
- Anhydrous sodium sulfate
- Dichloromethane

III. EXPERIMENTAL METHODOLOGY

In a 20 mL flat-bottomed ball flask, 5.3 mL of isoamyl alcohol was mixed with 7.3 mL of glacial acetic acid and a magnetic stirrer was added. The flask was held, centered on the wire rack, with the three-finger clamp, followed by gentle unheated shaking as indicated in Figure 3.1.



Figure 3.1. Stirring process without heating 5.3 mL of isoamyl alcohol with 7.3 mL of acetic acid.

1.2 mL of concentrated sulfuric acid (caustic) was evaluated, putting it in a dry test tube and using a Pasteur pipette, it was added to the flask mixture, drop by drop, stirring so that it dissolves as shown in Figure 3.2.



Figure 3.2. Measurement of concentrated sulfuric acid.

The flask and tube junctions were then cleaned and greased. refrigerant and the refrigerant was connected to the flask, placing it vertically. Reflux was carried out for an estimated time of one hour. During heating, the mixture turned brown as indicated in Figure 3.3 because some of the organic material was burned by heating with sulfuric acid; the blue or green colorations that were observed are due to the intermediate ions (oxonium ions and carbocations) that were formed during the reaction.



Figure 3.3. Reflux of organic material in the presence of sulfuric acid by heating

Later, when the reflux hour ended, the mixture was cooled so that the isolation of isoamyl acetate occurred as indicated in Figure 3.4, for this it was convenient to cool first in a water bath and then in an ice bath.



Figure 3.4. Cooling of the solution in a water bath and an ice bath.

The mixture was transferred from the flask to a separatory funnel which contained 10 mL of ice water. The flask was then rinsed with an additional 5 mL of ice water and added to the separatory funnel and then rinsed again with another 5 mL of water. Figure 3.5 shows the separation of the aqueous phase from the organic phase and subsequent elimination of the aqueous phase.



Figure 3.5. Separation of the organic phase and aqueous phase in a separatory funnel.

Next, 10 mL of a 10% sodium bicarbonate solution was added to the organic phase present in the separating funnel as shown in Figure 3.6 and the mixture was stirred, in this way the CO_2 formed could be released. A time was waited until the phases could separate and then the aqueous phase was removed.



Figure 3.6. Release of CO_2 from the organic phase after adding bicarbonate to the solution.

10 mL of the sodium bicarbonate solution was added again and the same operation was carried out until the aqueous solution had an alkaline pH of 8, which was light green on the pH paper. Then the organic layer was washed for the last time with 10 mL of 25% sodium chloride solution, and the separation was allowed to be maximum and the aqueous phase was completely removed. Subsequently, the organic phase was placed in a 25 mL Erlenmeyer flask and anhydrous sodium sulfate was added and the liquid was expected to come into contact with the drying agent for a time of 10 min. The solution, without the solid, was transferred using a dry Pasteur pipet to a round flask and then the sodium sulfate was washed with 2-3 mL portions of methylene chloride, to recover the isoamyl acetate that remained absorbed in the solid. A Magnetic stirrer in the distillation flask as indicated in Figure 3.7.



Figure 3.7. Magnetic stirrer placed in the solution in the distillation process.

Finally the product was distilled where the methylene chloride was distilled first but since its boiling point is very low it did not condense. The distilled product was received in

a 10 ml graduated cylinder and all temperature changes and the volume that distilled at each temperature were noted. When the temperature stabilized, the first drops of distillate were emptied into another container and in this way a purer product was obtained.

IV. RESULTS AND ANALYSIS

4.2 mL of isoamyl acetate were obtained, which is equivalent to 3,679 grams and the reaction presents a yield of 58.09%, in Annex 1 the yield calculations are observed and in Table 4.1 the initial data and results obtained are shown. in the process of synthesis of isoamyl acetate.

Table 4.1. Results obtained in the isoamyl acetate synthesis process

REAGENTS		PRODUCTS
Alcohol isoamyl	acetic acid	acetate isoamyl
Mw = 88 g/mol	Mw= 60 g/mol	Mw = 130 g/mol
V real = 5,3 mL	V real = 7,3 mL	V real = 4,2 mL
D= 0,81 g/mol	D = 1,05 g/mL	D = 0,87 g/mL
w= 4,29 g	w = 7,66 g	w= 3,67 g
Yield percentage		58, 09%

The yield percentage is relatively acceptable as observed in Table 4.1 because in practice there could be product losses due to the fact that paraffins were not possibly used to avoid the loss of some reagents due to gas emission, another cause could also be the moment of decantation that a little of the organic phase has gone into the aqueous phase or possibly that the water has not been completely eliminated causing a reversibility towards the reactants.

Another factor that could have affected the performance of the reaction is the catalyst used in the reaction, in this case it was sulfuric acid, so in subsequent practices it would be advisable to use other catalysts to verify their effectiveness and how they affect the performance of these types of reactions. In addition, in practice, excess acetic acid was added due to the fact that in the reaction there is isoamyl alcohol as a limiting reagent and is also a way to favor or benefit the ester, the same that allows a better shift of the reaction towards the formation of the ester, that is, it improves the yield. The literature mentions that in most esterification reactions it is advisable to add an excess of alcohol since excess acid can lead to separation problems due to the formation of azeotropes or the high consumption of alkali or base to neutralize the effluent of reaction (Jairo & Durán, 2013), if this had occurred the reaction would have caused a hydrolysis of the ester, having as products an alcohol and a carboxylic acid.

V. CONCLUSIONS

The isoamyl acetate synthesis process gave a yield value in the reaction of the 58.09%.

In the isoamyl acetate formation reaction, it was determined that the limiting reagent is isoamyl alcohol, while the excess reagent is glacial acetic acid, the same one that receives the nucleophilic attack of alcohol and is the molecule where the alcohol is created. leaving group (water) in the reaction.

Isoamyl alcohol, being the limiting reagent, allowed a better shift of the reaction towards the formation of the ester, which helped to improve the yield of the reaction.

Catalysts are of great importance in esterification reactions as they help protonation in the aqueous phase to achieve electronic delocalization and benefit the formation of the ester.

Sodium bicarbonate was necessary at the time of reacting with the acid, in order to neutralize the aqueous phase and help the formation of salts for its removal.

The isoamyl acetate obtained has a strong and characteristic banana odor.

To synthesize isoamyl acetate, it is not enough to run the mixture, it must be heated and then purified.

Sulfuric acid in this reaction acts as a catalyst.

The ester is obtained with a pH 8 in the organic phase which gave a light green color on the pH paper.

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