

Distillation of Reaction between Isobutyric Acid and Isobutyl Alcohol

Purpose:

Isobutyric acid was reacted with excess isobutyl alcohol and catalytic sulfuric acid to form isobutyl 3-methylpropanoate. The reaction was monitored with GC and worked up using liquid liquid extraction. Then, the product was isolated by simple distillation. Following purification, the product was characterized by ^1H NMR, IR, GC, and GC-MS spectral analyses. Distillation is an important technique used to separate mixtures of liquids with different boiling points. It was applicable in this reaction because the remaining alcohol reactant and ester product are both liquids with differing boiling points.

Results, Discussion, and Conclusion:

Esters are common organic compounds that can be synthesized through the reaction of a carboxylic acid and primary alcohol with a strong acid catalyst in a reaction known as Fischer Esterification, an equilibrium process. The forward reaction can be driven by the use of excess alcohol or the continual removal of water during the reaction (3). In this particular case, the reaction was driven by the use of excess isobutyl alcohol. The addition of a strong acid catalyst results in the protonation of the carbonyl oxygen on the carboxylic acid. The alcohol then performs a nucleophilic attack on the carbonyl, forming a tetrahedral intermediate. Then, proton transfer occurs by the alcohol proton detaching and attaching to the carboxylic acid oxygen, forming water as a substituent. A lone pair on the original protonated carbonyl oxygen forms a double bond with the geminal carbon, cleaving off the water molecule. The alcohol is then able to deprotonate the carbonyl hydrogen to yield the ester product and obtain the catalyst back.

In this experiment, isobutyric acid and isobutyl alcohol were chosen as the carboxylic acid and alcohol, respectively (1). The reaction was monitored with mini-GC, a chromatography procedure that was chosen as a replacement to TLC. TLC was not appropriate for this particular reaction because the reactants and products were both volatile and non-UV active. They therefore could not be visualized on a TLC plate. The mini-GC data indicates that the reaction may have gone to completion because after 60 minutes. The ester made up 95.9% of the reaction mixture while the excess alcohol made up only 4.9% of the mixture. However, the percent composition of the ester was still increasing up until the 60 minute time point, albeit at a slower rate, which suggested the formation of the ester was not complete (6). Nevertheless, more data would be needed to see if the reaction had indeed stopped, which would have been indicated by a stop in the increase of the percent composition of the ester.

The reaction was worked-up using sodium bicarbonate to quench the acid catalyst and remove unreacted isobutyric acid. Bicarbonate served as the base that deprotonates unreacted carboxylic acid starting material and draws it out of the organic ether solvent. The leftover organic layer contained any excess alcohol and ester product. In addition, bicarbonate is a weak base that does not react violently with the sulfuric acid. Therefore it was also chosen as a safety consideration in order to prevent the splashing of any acid or other chemicals. The neutralization reaction was confirmed by the observation of carbon dioxide bubbles evolving after the addition of the sodium bicarbonate solution (5).

Following the work-up, the ester product was purified of any excess alcohol by simple distillation. Though the conditions for simple distillation were not met since the boiling point of the alcohol (108 °C) and ester (149 °C) differ by less than 75 °C, the procedure was still

appropriate because of the relatively small proportion of alcohol present in the mixture (1). After 60 minutes, alcohol only made up 4.9% of the mixture (6). Therefore it could easily be distilled to a pure product by simple distillation. The observed boiling points of the ether solvent, alcohol, and ester were 35-72 °C, 81-129 °C, and 130 °C and above, respectively. The corrected boiling point that adjusted for differences in atmospheric pressure were 35.35-72.35 °C, 81.35-129.35 °C, and 130.35 °C and above, respectively. However, the percent yield was fairly low (44.6%). This low percent yield was likely due to an incomplete reaction, which would have left some of the carboxylic acid unreacted and incomplete formation of the ester product. Some more product may have been lost in the distillation procedure as well, as the alcohol and ester collection vessels may not have been switched soon enough, resulting in some ester product being collected with the alcohol. Nevertheless, no glaring deviations from the expected occurrences occurred during the distillation, so it therefore seemed to be largely successful.

The ¹H NMR spectrum of the product indicates that the expected ester product indeed formed although slight alcohol impurities were present. Characteristic isobutyl and isopropyl splitting was present, with two large, upfield, 6 hydrogen doublets and corresponding 1 hydrogen multiplets shifted downfield and adjacent to the doublets. A 2 hydrogen doublet is present and shifted downfield (3.9 ppm), which corresponds to the two secondary hydrogens on the isobutyl group of the ester. Two small impurity peaks were visible on the ¹H NMR spectrum, both likely from the alcohol starting material. First, a short but broad downfield peak (5.9 ppm) corresponds to the hydrogen on the alcohol functional group. Second, a small doublet peak (3.4 ppm) corresponds to the methyl hydrogens of the isopropyl group on isobutyl alcohol. In The IR spectrum, sharp peaks were visible at 2971.29 and 2876.76 cm⁻¹, corresponding to the various

C-H bonds in the ester product. A sharp carbonyl peak was visible at 1734.40 cm^{-1} and an ester C-O peak was visible at 1154.34 cm^{-1} . The combination of the peaks supports the expectation that an ester was formed by this reaction.

A final GC analysis and GC-MS analysis were performed on the ester distillate, and the percent composition of the ester was calculated to be 95.17% with a retention time of 10.977 minutes while the final percent composition of the alcohol impurity was 4.83% (4). This GC data supports the ^1H NMR and IR data that indicates the ester was formed with alcohol impurities, given that the ester makes up the majority of the final distillate and alcohol makes up a small proportion. However, one problem with this GC data is that the mini-GC data taken during the reaction actually showed that the final percent composition of the ester was 95.1%, which is very close to the final percent composition of the ester based on the final GC analysis. Therefore, the distillation seemed to not have purified the product very well at all. In the GC-MS data for the ester product, only one peak was observed. Therefore, the composition of the product was extremely pure. The mass spectrometry spectrum also supports the ^1H NMR and IR data, since the fragmentation pattern matches the expected fragmentation pattern of the ester product (2). First, an isobutyl group cleaves off, then a secondary carbon, followed by a single oxygen, and a methyl group, which leaves behind the final fragment.

In this experiment, excess isobutyl alcohol and isobutyric acid were reacted to successfully form isobutyl 3-methyl propanoate. The product mixture was then purified by simple distillation with some success. Though ^1H NMR and IR spectral analyses showed that the product was indeed formed, GC data suggested that the product was impure and contained excess unreacted alcohol starting material. In order to further purify the product, simple

distillation may not have been appropriate, and fractional distillation would be the biggest improvement on the percent yield. Fractional distillation may have also helped improve the percent yield of the ester product. Several sources of error were also present in this procedure, namely in details such as not distilling to completion as a safety concern, the reaction not going fully to completion, and the use of simple distillation on a mixture of liquids with close boiling points.

Experimental:

Isobutyric acid (7.5 mL) and isobutyl alcohol (10 mL) were added to the reaction vessel. Concentrated sulfuric acid (5 drops) was added to begin the reaction. A reflux apparatus was attached to the reaction vessel and the reaction was stirred and heated gently for 30 minutes. Next, a small sample (0.5 mL) of the reaction mixture was added to 10% aqueous sodium bicarbonate (15 drops) and 3M aqueous sodium hydroxide (15 drops). The top layer was used in mini-GC analysis and the reaction was allowed to run for another 30 minutes. The reaction mixture was extracted with ether (2 x 10 mL), 5% aqueous sodium bicarbonate (4 x 10 mL), distilled water (1 x 10 mL), and saturated sodium chloride (1 x 10 mL). Next, the reaction mixture was dried over anhydrous sodium sulfate. A simple distillation apparatus was then set up. The mixture was stirred and heated gradually and three distillates, ether, alcohol, and ester, were collected at three different temperature ranges. ^1H NMR (60 MHz, deuterated chloroform) δ : 0.8-1.1 (d, 6H), 1.1-1.4 (d, 6H), 1.5-2.1 (m, ^1H), 2.5-2.8 (m, ^1H), 3.8-4.0 (d, 2H). IR ν_{max} (cm^{-1}) 2971.29, 2876.76, 1734.40, 1194.15, 1154.34. GC (phenyl methylpolysiloxane, 40 °C to 125 °C at 5 °C per min) RT 2.849, 10.902. GC-MS (phenyl methylpolysiloxane, 40 °C to 125 °C at 5 °C per min) RT 10.92 min, m/z 145.33.

References:

- (1) Dykstra, S.; Beiswenger, K; Bischof, A. *Lab Guide for Chemistry 213W Introductory Organic Chemistry Laboratory, 2017-2018.*; Macmillan Learning Curriculum Solutions: Michigan, 2018; pp 181-217.
- (2) Dykstra, S. *GC-MS data of isobutyl 3-methylpropanoate*
- (3) Libretexts. Fischer Esterification
https://chem.libretexts.org/Core/Organic_Chemistry/Carboxylic_Acids/Reactivity_of_Carboxylic_Acids/Fischer_Esterification (accessed Feb 28, 2018).
- (4) Lind, Michael. *GC Data of Ester Distillate*
- (5) Sodium bicarbonate https://pubchem.ncbi.nlm.nih.gov/compound/sodium_bicarbonate (accessed Feb 28, 2018).
- (6) Thoma, B. and Vera, Lara. *Mini-GC data for Reaction between Isobutyric acid and Isobutyl Alcohol.*