

Synthesis of n-Butyl Acetate

Barbara Jennings

Chem 203.1

Desk 109.D

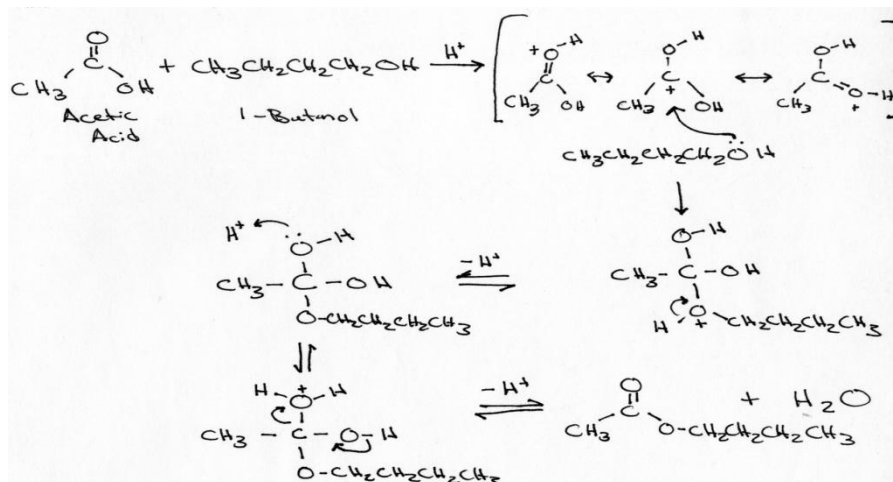
Ta: Tian Chen

Introduction:

An ester group is an important functional component in many chemical compounds such as fatty acids and components of fragrances and flavors. Esters are widespread throughout nature, but are also a vital use in industry. The synthesis of low molecular weight esters, by the reaction of a carbonyl with an alcohol, is essential to the fragrance and flavoring industry. n-Butyl acetate is a widely known ester used as a solvent in the production of lacquers, but more commonly as a synthetic apple flavoring used in foods such as ice cream, candy, jams, and baked goods.

n-Butyl acetate is synthesized by reacting acetic acid with n-butanol and p-toluenesulfonic acid catalyst. This reaction is an example of a Fischer esterification or a nucleophilic acyl substitution mechanism. The reaction precedes by protonating the carbonyl oxygen of acetic acid with the catalyst p-toluenesulfonic acid. A resonance hybrid is formed upon protonation and the resonance form that contains the electrophilic carbon is easily attacked by the nucleophilic oxygen of the alcohol 1-butanol. The final product is formed by the removal of a water molecule and subsequent deprotonation of the attached alcohol. The water is physically removed as an azeotrope by distillation in a modified Dean-Stark apparatus. It is important to remove the water so the reaction mixture will not reach equilibrium. By Le Chatelier's principle, if the water is continuously removed the reaction must continue to drive forward producing pure n-butyl acetate.

Figure 1: Mechanism for the Synthesis of n-Butyl Acetate from the Reactants Acetic Acid and 1-Butanol



Experimental:

Rinsed Dowex 50 x 2-100 ion-exchange resin (0.2g), acetic acid (0.61g, 10.16 mmol), 1-butanol (0.74g, 9.98 mmol), and a 1/2" stir bar were added to a 5-mL short-neck round-bottom flask. The distillation head was equipped with a 3-way connector fitted with a plug. The reaction mixture was stirred over a hot sand bath and allowed to reflux for 30 to 40 minutes. The azeotrope collected in the sidearm of the 3-way connector and the two layers separated. The top layer (ester) is decanted back into the reaction flask and the bottom layer (water) is left in the 3-way connector. The product was removed from the reaction flask by Pasteur pipet filtration and then weighed. n-Butyl acetate was isolated as a clear, slightly yellow liquid (1.169g, 85.9% yield) with a fragrant apple smell. The sample was then prepared for analysis and nuclear

magnetic resonance (NMR), infrared spectroscopy (IR), and gas chromatography (GC) spectrums were obtained.

Results:

Observed Shift (ppm)	Observed Splitting	Observed Integral	Type of Hydrogen(s)
0.75-1.9	multiplets	10.76	-CH ₂ CH ₂ CH ₃
2.1-2.2	doublet	4.2	-CH ₃ and acetone impurity
3.5-3.8	multiplet	0.59	H-O-CH ₂
3.9-4.28	triplet	2.00	-O-CH ₂ -
5.2-5.45	Singlet	1.36	-OH

Table 1: NMR data obtained for reaction sample (3 drops) with deuterated chloroform solvent on a 60 MHz NMR.

Observed	Bond Stretch
2945.6 cm ⁻¹	-C-C-
1724.0	R-CO-OR

Table 2: Significant signals for IR data for reaction sample.

Observed Retention Time (min)	Observed Area
1.66	961020
2.51	15201
6.03	18876

Table 3: Significant signals for GC data of reaction sample.

Discussion:

From the analytical data, it was shown that the final product was not 100% pure n-butyl acetate. The NMR data of the reaction sample showed the exact chemical shifts that would have been seen for a pure sample of n-butyl acetate: multiplet 0.75-1.9 ppm, doublet 2.1-2.2 ppm, and triplet 3.9-4.28 ppm. However, the integral values of these chemical shifts were slightly higher than expected for a pure sample of n-butyl acetate, indicating that the sample was not completely pure and contained some starting materials and impurities. For example, the 0.75-1.9 ppm chemical shift represented the $-\text{CH}_2\text{CH}_2\text{CH}_3$ portion of n-butyl acetate and should have shown an integral value of 7. However, the observed integral value was 10.76. Since the starting material 1-butanol contains the exact same $-\text{CH}_2\text{CH}_2\text{CH}_3$ portion in its structure, with a similar chemical shift pattern as the $-\text{CH}_2\text{CH}_2\text{CH}_3$ portion of n-butyl acetate, the higher integral value is intuitive of overlapping signals from both the product and reactant. It is important to note that if both the reactant and product were in equal concentrations, the 0.75-1.9 ppm multiplet stretch would theoretically have an integral value of 14, but actually displayed an integral value of 10.76. Since the integral values were based on the stronger concentrated product n-butyl acetate, the reactant (present lower concentrations) only exhibit a fraction of the integral value it theoretically would have shown if it were in equal concentrations with the product. Thus the integral of the chemical shift 0.75-1.9 showed an integral value of 10.76 instead of an integral value of 14. This indicates that even though the final product was not pure n-butyl acetate, there still was a higher concentration of n-butyl acetate to the reactants.

Further analysis of the NMR data confirmed the presence of reactants and impurities. For example, the doublet at 2.1-2.2 ppm should theoretically have been a singlet, but since the NMR tube was not completely dry from washing it with acetone, an acetone peak (commonly around

2.17 ppm) occurred in the same region making the peaks appear to be a doublet. Another triplet was observed around 3.5-3.8 ppm with an integral value of 0.59. This small integral value and shift indicates that the O-CH₂ hydrogens of the reactant 1-butanol was present but at a much lower concentration as compared to the product. Finally, the integral value of 1.36 at 5.2-5.4 ppm confirmed that the reactant 1-butanol was definitely present since these observed values represent the HO- of its structure.

The IR data contained a 2945.6 1-cm stretch prevalent of all chemical compounds containing -C-C- stretches. The 1724.0 stretch confirmed that the product was present by indicating the ester functional group R-CO-O-R.

The GC data was a near perfect match to a theoretically pure n-butyl acetate GC data. The retention times (RT) at 1.66 and 6.03 nearly matched the pure standard data with RT at 1.60 and 5.05. The sample data peak areas were less than that of the standard data with an area of 961020 at RT 1.66 and area of 18876 at RT 6.03 as compared to the pure n-butyl acetate data with an area of 260E8 at RT 1.60 and area 990616 at RT 5.05. This indicates that there was a weaker concentration of n-butyl acetate in the sample as compared to pure n-butyl acetate. The other significant peak at 2.51 with an area of 15201 confirmed that reactants were presents in the sample.

Conclusion:

Overall, the techniques used to analyze the sample proved effective at confirming that both reactants and products were present in the sample. The NMR and GC data were helpful at indicating that the product n-butyl acetate was presented in a higher concentration than the reactants. The NMR data also helped confirm other impurities, such as acetone. The IR data

significantly confirmed that the ester n-butyl acetate was present. The techniques used to obtain pure n-butyl acetate from the distillation of the reaction mixture acetic acid and 1-butanol did not prove to be effective. The modified Dean-Stark apparatus did not remove as the azeotrope containing the water effectively. Some water may still have condensed back into the reaction mixture creating an equilibrium and thus stopping the reaction from moving forward and producing 100 % pure n-butyl acetate. For future work, a liquid-liquid extraction could have been used to isolate pure n-butyl acetate from the reaction sample.

References:

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