Greener Fragrances: Triethylammonium Hydrogen Sulphate $[TEA][HSO_4]$ as a Greener Catalyst

The Institute for Research in Schools

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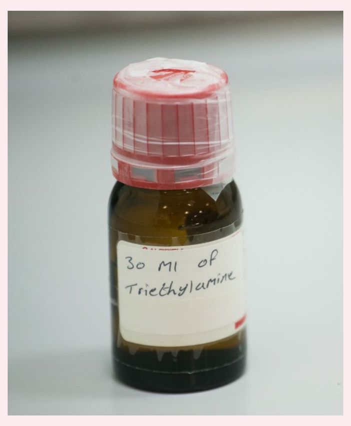
Research Aims

The aim of our research is to investigate how effective triethylammonium hydrogen sulphate is as an environmentally friendly catalyst compared to other harmful catalysts, like sulfuric acid.

Introduction

Traditionally, esterification has been catalysed using an inorganic acidic catalyst, but in recent years, ionic liquids have been gaining attention as a potential alternative to these traditional catalysts or solvents. Acids like sulfuric acid or hydrochloric acid have been used due to their ease of access and low price point, however ionic liquids have a wide range of unique properties which could make them a better option for many applications, such as low volatility, high selectivity and recyclability. Ionic liquids[1] are organic salts that stay in a liquid state at room temperature.

In this project, the possibility of ionic liquids being a better solution for catalysing esterification reactions is explored to investigate the possibility of them being a greener, more sustainable alternative to acidic catalysts.



Images 1-3 left to right: 1: preparing the ionic liquid; 2: the TEA used and 3: preparing an ester

Experimental Method

Ionic Liquids:

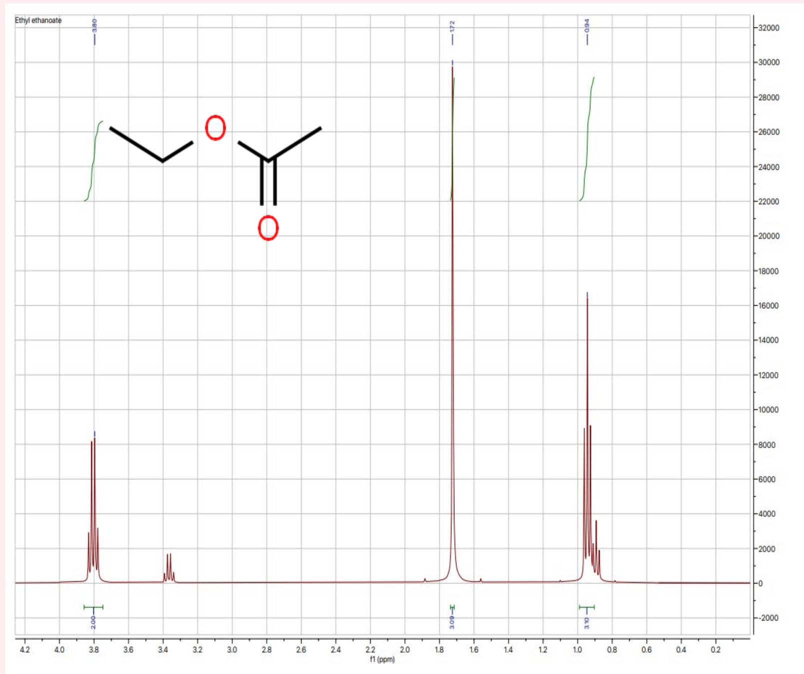
- 40g of 0.20001 mol ionic liquid was made to act as a catalyst for esterification.
- Triethylamine was weighed into a round bottom flask and reacted with sulphuric acid, added drop-by-drop using a glass pipette while cooled on ice.
- An observable colour change from pale yellow to brown was seen, upon which the flask was removed from the ice bath and stirred for a further 2 hours.

Esterification:

- 0.1 mol carboxylic acid was weighed into a round bottom flask using an analytical balance and 3g ionic liquid catalyst added to it and mixed.
- The alcohol was weighed out to ensure a 1:1 molar ratio to the acid, added to the flask and mixed before adding a condenser to reflux.
- The mixture was heated to boil and then heat reduced to keep on a simmer for 10 minutes.
- The resulting mixture was added to a separating funnel to remove the ionic liquid and any water produced as a by product. The ionic liquid was retained to reuse as a catalyst in another synthesis.

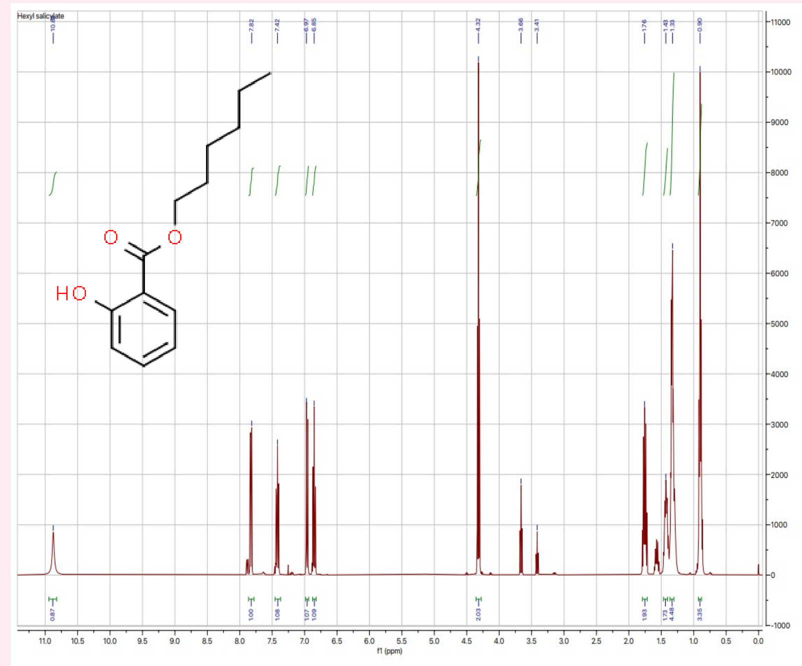
Results

Spectra shown below are Proton NMR spectra for of a range of esters synthesised using the Ionic Liquid catalyst with the ester structure[2] included.



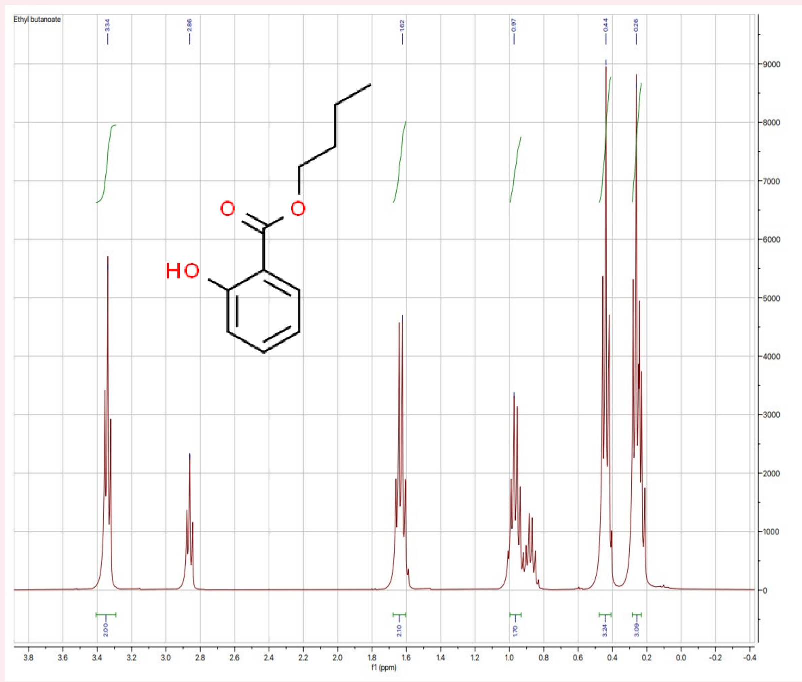
<u>Figure 1: Ethyl ethanoate</u>

Yield by NMR analysis= 93.42%



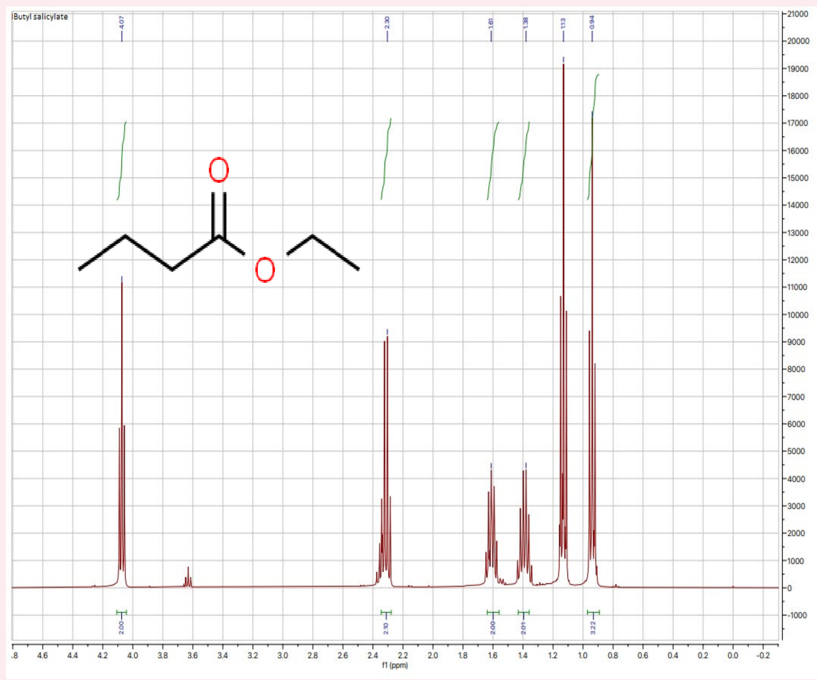
<u>Figure 2: Hexyl salicylate</u>

Yield by NMR analysis = 67.63%



<u>Butyl salicylate</u>

Yield by NMR analysis = 87.45 %



<u>Ethyl butanoate</u>

Yield by NMR analysis= 92.98 %

Analysis & Conclusions

- The NMR analysis showed the ester synthesis was not just successful using the ionic liquid as a catalyst but that the percentage yield was higher than using the traditional acidic catalyst when comparing to ethyl ethanoate prepared using a sulphuric acid catalyst and otherwise the same conditions (93.42% compared to 65%[3]). As we increased the volume of ionic liquid catalyst added to the esters from 0.3g to 3g, the reaction sped up considerably from ~8h to ~1h, proving the ionic liquid catalyst was effective. However, NMR did indicate the presence of an impurity even with using the ionic liquid as the catalyst so further analysis by GC-MS would be recommended to clearly identify if the impurity was due to unreacted reactants.
- One noticeable difference observed across the results is that the esters made with two liquid reactants were more time and energy efficient. The reaction of the ester salicylates did not fully react despite more time, energy and ionic liquid catalyst being used in effort to complete the reaction. The aromatic component of salicylic acid was thought to be the cause of the problem and would require consideration in terms of method development before any further synthesis attempted. The ethanoic acid doesn't have an aromatic component in addition to being in the liquid state therefore having more energy as a reactant than the salicylic acid. This meant less energy in the form of heat and kinetic energy were necessary to complete the reactions. Use of ionic liquids in industrial production of esters and whether it would be a profitable or realistic alternative to traditional catalysts used in industry remains a query given inconsistent results depending on the state of matter of the reactants.

Future Development Work

- Find a way to make solid esterification work - possibly dissolving solid acids before esterification to reduce additional heat energy needed for state change in the reaction.
- Ratios of catalysts to solid and liquid reactants to find the most efficient ratio and time how long it takes to determine efficiency.

References:

1. Tom Welton (2004) Ionic liquids in catalysis, Coordination Chemistry Reviews. Available at: https://www.sciencedirect.com/science/article/abs/pii/S0010854504001183 (Accessed: 22 May 2023).
2. https://www.chemspider.com (all chemical structures)
3. https://www.chemicalbook.com/ChemicalProductProperty_EN_CB7255315.htm (Typical yield with sulphuric acid catalyst)

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