

Ionic Liquids

To improve the action and efficiency of catalysts

Dixons Sixth Form
Academy

Research Overview

Students from Dixon's Sixth Form Academy are keen to improve how chemistry and the chemical industry are perceived by the general public. Often chemistry is seen as harmful and something which causes pollution and contributes to climate change however there is a great emphasis on improving chemical processes. Due to disruptions to attempts at conducting primary research caused by the on-going pandemic this poster demonstrates how ionic liquids can be used to improve reaction yields and help traditional chemistry reactions by acting as catalysts reducing the need to large amounts of energy and speeding up reactions.

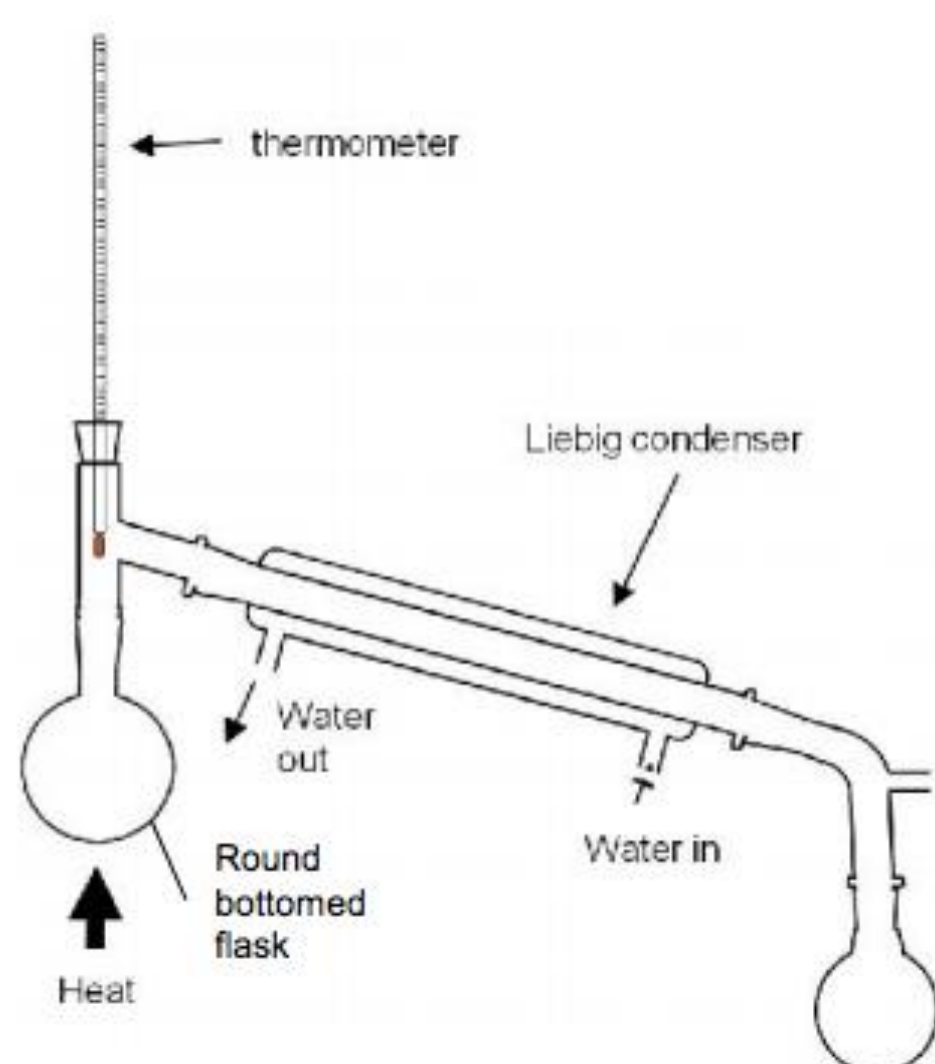
What are Ionic Liquids? And what makes them suitable for this purpose?

Ionic liquids are a fascinating class of compounds that are widely regarded as excellent alternatives to standard solvents. Because these compounds have low vapour pressure and can resist the severe conditions of space, they have been utilised in a variety of specialty applications, including the catalyst industry, which is what we have theoretically investigated. Ionic liquids are ionic compounds with large asymmetric ions that prevent the lattice from forming. Table salt, sodium chloride, is the most common example of an ionic compound; however, because of the regular arrangement of ions in its structure, it is a solid, crystalline substance. Scientists are interested in these because they share similar features to traditional ionic compounds. They can be understood as a salt in a liquid state below 100 degrees Celsius. They have great qualities such as being volatile and non-flammable that would help make them much safer to use.

Qualities of ionic liquids that allow them to be useful for this purpose:

Ionic liquids often have more resistance to decomposition at high temperatures. They are also non-volatile and non-flammable but ignite when they contain high energy moieties (branches in organic molecules that extend from the carbon backbone and is part of a molecule that is connected to another molecule) e.g., nitro groups. They also ignite at temperatures near to their decomposition temperature. Therefore, the more thermally stable an ionic liquid, the less likely it is to ignite. Not only does this improve the recovery and reuse of the ionic liquid after a reaction, limiting waste, but also improves the safety of chemical processes.

Reference: McNeice, P., Marr, P.C. and Marr, A.C. (2021). Basic ionic liquids for catalysis: the road to greater stability. *Catalysis Science & Technology*, 11(3), pp.726–741. doi:10.1039/d0cy02274h.



Reference "1. AQA Revision Guides." *Chemrevise*, chemrevise, 3 Mar. 2019, chemrevise.org/revision-guides/.

The apparatus was set up as seen in the picture and used to synthesise ethyl ethanoate. In a fume cupboard ethanol and glacial ethanoic acid was mixed thoroughly in a round-bottomed flask. In a fume cupboard, concentrated sulfuric acid was added dropwise. This is an exothermic reaction and was therefore done slowly. Concentrated Sulfuric acid is highly corrosive and so to ensure safety, latex gloves were worn. Some anti-bumping granules were added and then fit to the flask to distillation apparatus. About two-thirds of the mixture were distilled off. The boiling point of the liquid that comes off was measured. The distillate was transferred to a separating funnel. Water was added. The funnel was stoppered, inverted, and shook, opening the tap from time to time. The two layers were separated, and the lower layer was run off and rejected, ensuring that the sodium carbonate was removed as completely as possible. The process was repeated with 30% sodium carbonate solution. The ethyl ethanoate was poured into a beaker, and a spatula of anhydrous magnesium sulfate was added and stirred well. The magnesium sulfate clumped together with any water in the mixture. When there is free moving powder in the flask, all the water was removed. It was left to settle then the ethyl ethanoate was decanted into a flask. The amount of ethyl ethanoate produced was measured, and a percentage yield was calculated.

Evidence for use of Ionic Liquids in catalysis

Esterification

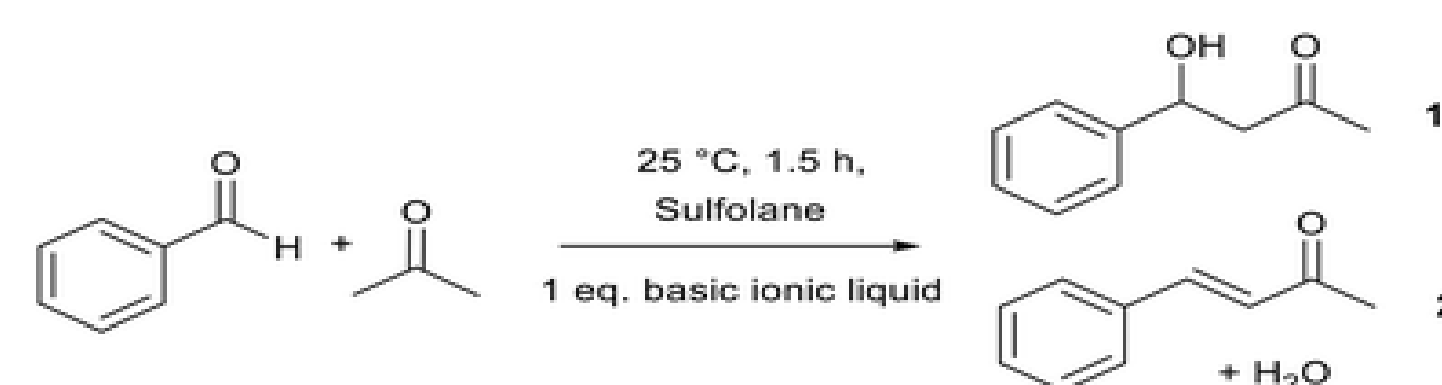
Acetates are chemicals that play a vital role in the modern chemical industry for example in the textile industry and solvent extraction in pharmaceutical industry. Esterification of alcohols with carboxylic acids is one of the most important reactions to obtain acetates. However, esterification uses the catalyst sulphuric acid which is strongly corrosive making this reaction potentially environmentally problematic. When using the ionic liquid aluminium chloride 1-butylpyridinium chloride–aluminium(III) chloride for the esterification of 2 propanol researchers found the ionic liquids produced 71.3 conversion compared to 66.2 using sulphuric acid.

Reference: Y. Deng et al. / *Journal of Molecular Catalysis A: Chemical* 165 (2001) 33–36

1) Adol condensation

Adol condensation reactions are important as they form C–C bonds in organic chemistry. Usually, these reactions are catalysed by aqueous NaOH, however this is unsustainable as it can lead to reactor corrosion and the production of salt waste. McNeice, A. C. Marr, P. C. Marr, M. J. Earle and K. R. Seddon investigated binary alkoxide ionic liquids such as ([Pyrr1,4][NTf2]_x[OiPr]_{0.43}) catalysed the adol condensation between propanone and benzaldehyde. This reaction is a suitable model for the condensation between furfural and propanone which could be an important step in upgrading lignin and cellulose to valuable chemicals. This is one way the application of binary alkoxide can be useful. The ionic liquid that gave the best result, ([Pyrr1,4][NTf2]_{0.57}[OiPr]_{0.43}) achieved a higher yield (75%) than when NaOH was used (69%). The total yield increased from 12% to 75%, while the yield of unsaturated ketone product 2 increased from 8% to 60% when a higher proportion of alkoxide anion was present in the ionic liquid. This highlights how extreme of an impact these ionic liquids can have on the yield of the reaction product.

The reaction mechanism for this is shown below. It shows the adol reaction catalysed by binary alkoxide ionic liquids

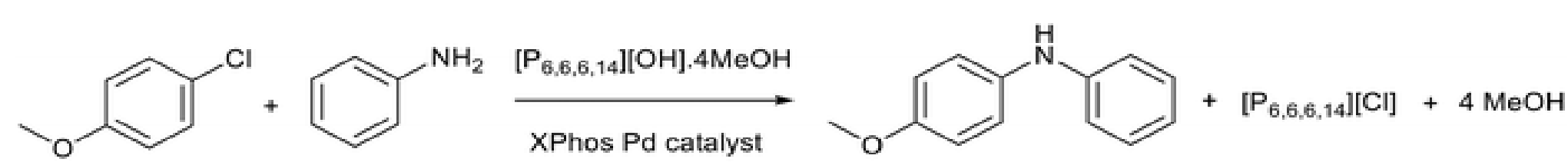


Reference: P. McNeice, A. C. Marr, P. C. Marr, M. J. Earle and K. R. Seddon, *ACS Sustainable Chem. Eng.*, 2018, 6, 13676–13680

2) Metal Catalysed reactions

Trihexyl-tetradecyl phosphonium hydroxide has very high stability. This means it can be used in metal-catalysed reactions. Researchers "Rogers and co-workers" used this along with methanol as a basic promoter for cross-coupling reactions. This is a reaction in which two fragments are joined together with the aid of a metal catalyst. These reactions are important as they can create C-C, C-N, and C-O bonds. The methanol interacted more strongly with the protons, therefore the ionic liquid Trihexyl-tetradecyl phosphonium hydroxide is less likely to attack the cation to cause it to break down. The researchers had found that another advantage of this was that it prevented salt build-up. The use of the ionic liquid as base and solvent in this batch reaction, the yield for Suzuki–Miyaura reactions could reach 56%. The authors stated that under flow conditions the basic ionic liquid could be regenerated and reused. Therefore, acting much like a catalyst. In the mechanism for any organic reaction, C-O, C-C and C-N bonds are made and broken.

The mechanism for the reaction is shown below. It shows an example of a Buchwald–Hartwig cross-coupling using [P_{6,6,6,14}][OH]·4MeOH as a base and solvent:



Reference: H. Choudhary, P. Berton, G. Gurau, A. S. Myerson and R. D. Rogers, *Chem. Commun.*, 2018, 54, 2056–2059

