JoVE: Science Education

Driving Equilibria: Dean-Stark Trap

--Manuscript Draft--

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Science Education Title: Driving E~~e~~quilibria: Dean-Stark T~~t~~rap

Overview

A Dean-Stark trap is a special piece of glassware, which allows the collection of water during a reaction through an azeotropic distillation. The desire to collect water from a reaction can have various reasons. It can drive the equilibria in reactions, where water gets formed as a byproduct. According to Le Chatelier's principle a change in temperature, pressure, concentration, or volume will cause a readjustment of a reversible reaction to establish a new equilibrium. An acetal formation ~~esterification~~ is a reversible reaction, where water gets formed as a byproduct. In such cases, achieving good yields is possible by driving the equilibrium towards the product side via the removal of water. The Dean-Stark trap also allows the determination of water content or can be used to remove water from a solvent mixture through an azeotropic distillation. ~~According to Le Chatelier's principle a change in temperature, pressure, concentration, or volume will cause a readjustment of a reversible reaction to establish a new equilibrium. An esterification is a reversible reaction, where water gets formed as a byproduct. In such cases, achieving good yields is possible by driving the equilibrium towards the product side via the removal of water. The Dean-Stark trap is a specialized piece of glassware commonly employed to achieve condensation reactions, where water gets formed as a byproduct.~~

Principles

A reaction equilibrium can be influenced ~~by using~~with an excess of reagent or removal of ~~the~~ a formed product in order to drive the equilibrium to the product side. Equilibria can be also influenced by temperature or pressure. This underlying principle is called Le Chatelier's principle and states that a change in temperature, pressure, concentration, or volume will cause a readjustment of the reaction to establish a new equilibrium. By adding an excess of reagent the concentration changes and a new equilibrium establishes, favoring the product side. For instance, ~~D~~driving the equilibrium of a hydrolysis can be easily achieved by adding an excess of water.

Influencing the equilibrium of a reaction where water gets formed as a byproduct, like an esterification, is not as straightforward and requires special glassware. This special piece of glassware is called a Dean-Stark trap and helps to remove the formed water from the reaction medium. Solvents that form an azeotrope with water, like toluene, are commonly employed. An azeotrope is a point in a distillation, where the composition of the liquid phase is equal to the composition of the gas phase. A further separation through a simple distillation past the azeotropic point is not possible. This is an advantage when using the Dean-Stark trap to influence equilibria, because it will ensure the continuous removal of water. Upon heating the reaction mixture, the formed toluene/water azeotrope will distill over, condense in the condenser, and flow into the Dean-Stark trap. Toluene and water will form two separate layers with toluene being the top layer and water being the bottom layer. While toluene can flow back into the reaction flask, water gets trapped as the bottom

Commented [ASW1]: It seems like more resources use the term “Apparatus” than “Trap”. Do you have an opinion between the two?

Commented [JR2R1]: That is a good point. Dean Stark Trap seems to be more common to me. When I look for “Dean Stark Trap” on SciFinder I get 528 hits, whereas for “Dean Stark Apparatus” I only get 13 hits. It appears to me, that “Dean Stark Trap” is more common on the academic/patent literature.
In google search I get 189k hits for “Dean Stark trap” and 71k hits for “Dean Stark apparatus”

Commented [ASW3]: This Overview focuses on one aspect of the trap: pushing reaction equilibria. It should focus on the more general use: collecting water during a synthesis. It can then include the reasons one would do this: pushing equilibria, determining water content, azeotropic distillations, etc.

Commented [ASW4]: Expand on this point. What is an azeotrope, and how does it help in this case.

layer and ultimately removed from the reaction equilibrium thus driving the reaction towards the product side.

Commented [ASW5]: I don't know this glassware very well. Does the water/toluene have to fill the apparatus to the side-arm before the toluene will re-enter the RBF?

Commented [JR6R5]: Yes, that's correct

Procedure

1) ~~Ester Formation~~Preparation
   a) Take a 250 ml round-bottom flask with a magnetic stir bar inside
   b) Place an oil bath under the round-bottom flask on a magnetic stirrer
   c) Fill the round-bottom flask with 7.5 g (0.05 mol) *m*-Nitrobenzaldehyde and add 75 ml of toluene
   d) Add 3.1 ml (3.45 g, 0.055 mol) ethylene glycol
   e) Attach the Dean-Stark trap to the round-bottom flask
   f) Attach a reflux condenser on top of the Dean-Stark trap
2) Running the reaction
   a) Set the oil bath temperature to 170 °C and heat the reaction mixture to reflux
   b) Monitor the reaction by measuring the water amount in the Dean-Stark trap
   c) The reaction is done when no further water gets trapped in the side arm of the Dean-Stark trap
   d) after approx. 2 hours the total amount of collected water is approx. 0.8 ml
3) Workup
   a) Release the water and remove the combined organic solvent from the reaction mixture under reduced pressure in a rotary evaporator
   b) Dissolve the yellow residue in 8 ml ethanol under reflux
   c) Cool down the solution
   d) The desired acetal will crystallize
   e) Filter the solid and dry it under reduced pressure

- ~~Assembly of the Dean-Stark apparatus~~
- ~~Add carboxylic ester and alcohol and solvent~~
- ~~Heat the reaction~~
- ~~Measure the amount of the trapped water to determine the reaction progress~~

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Commented [ASW7]: This Procedure doesn't have enough granularity. Each of these points should be expanded upon, explaining how they are carried out in more detail. See the other submitted manuscripts for examples.

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Representative Results

Water will form and gets trapped over the course of the reaction. The theoretical amount of formed water upon complete conversion can be calculated and compared with the measured amount of the trapped water to determine the reaction progress.

Summary

This experiment demonstrates in a vivid way Le Chatelier's principle and how it can drive an equilibrium.

Applications

Dean-Stark traps are commonly used to remove water from a solvent mixture. There are several reasons why it might become necessary to remove water from a solvent mixture. A simple reason is the removal of water through a simple distillation, when water does not form an azeotrope with the other solvent. In this case the design of the Dean-Stark trap allows the removal of water. In the case of an azeotropic distillation the addition of an entrainer is necessary. An entrainer is an organic solvent, which will form an azeotrope with water but does not mix with water in the liquid phase. The addition of an entrainer ensures the continuous removal of water, which again gets trapped in the side arm of the Dean-Stark trap. In a normal distillation apparatus, the continuous addition of an entrainer is necessary, since the distilled entrainer can't flow back to the solvent mixture. ~~i~~ The Dean-Stark trap can also be used to drive the equilibria of ~~n~~ reactions, where water gets formed as a byproduct, like in an ester or acetal formation~~, to drive the equilibrium towards the desired product~~. Through an azeotropic distillation where the solvent is also the entrainer removes water from the reaction and therefore from the equilibrium. Finally, an azeotropic distillation with a Dean-Stark trap can also be used to determine the water content of solvents or solvent mixtures. Not only water can be removed with a Dean-Stark trap but also ~~It can be also used to remove~~ volatile alcohols by placing 5-Å ~~A~~ molecular sieves in the trap.

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Commented [ASW8]: Like the Procedure, this is a bit terse. Flush it out to its logical conclusion. Also, please add additional uses of the glassware. From my research, this can include determining water content and azeotropic distillations.

Legend

Figure 1.~~:~~ Dean-Stark apparatus

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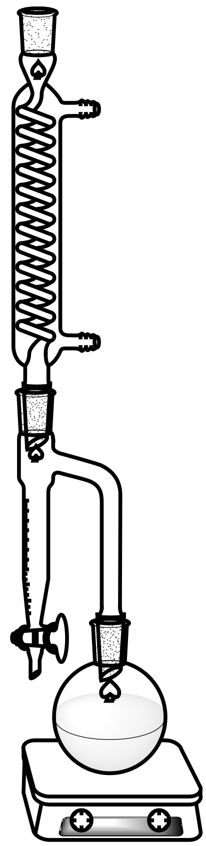

Figure 1