Esterification - Determination of Keq for the Acid-Catalyzed Esterification of 3-Toluic Acid with Methanol

Adapted by R. Minard and D. Dorisio (Penn State Univ.) from a microscale procedure used by the University of California, Irvine, in its undergraduate labs.

The procedure is based on an experiment introduced to the UCI Organic Chemistry Laboratory Program in the early 1970's by Marjorie C. Caserio, Professor of Chemistry. This procedure is a further adaptation by Kurt Rublein. Revised 10/10/00

Introduction

The purpose of this experiment is to determine Keq for the reaction:

\[
\begin{align*}
3\text{-toluic acid} & \quad \text{CH}_3\text{OH} & \quad \text{methyl m-toluate} \\
(3\text{-methylbenzoic acid}) & \quad \text{H}_2\text{SO}_4 & \quad (\text{methyl 3-methylbenzoate}) \\
\end{align*}
\]

This can be accomplished by knowing the exact amounts of reactants and by recovering and weighing unreacted 3-toluic acid after equilibrium has been reached.

\[
K_{eq} = \frac{[\text{H}_2\text{O}]}{[\text{CH}_3\text{OH}]} \frac{[\text{H}_3\text{C}O\text{CH}_3]}{[\text{H}_3\text{C}O\text{H}]} 
\]

The success of this experiment depends on quantitative recovery of the 3-toluic acid. Therefore, care should be taken that no spills occur during the liquid/liquid extraction procedure.

Prelaboratory Exercises

Prepare a liquid/liquid extraction scheme or flow chart for the separation and isolation of the unreacted 3-toluic acid from the equilibrium reaction mixture. Write the chemical formulae of the chemicals contained in the centrifuge tube, flask or vial, reaction tube, or test tube at each point in the scheme.

TLC

You are required to run a TLC to monitor the progress of the reaction. Plates should have three spots (or lanes) on the origin: one for the main organic starting material that is being transformed, one for a cospot (starting material and the reaction mixture), and one for the reaction mixture.

Experimental Procedure

Place 0.280 g of 3-toluic acid, 0.630 mL of anhydrous methanol (Hooded Shelf), 2 drops of concentrated H\textsubscript{2}SO\textsubscript{4}, and a boiling chip in a reaction tube. Use the connector with support rod to attach an air condenser, and cap the top of the condenser tube with a septum. BEFORE YOU START HEATING, pierce the septum with an empty syringe needle and leave it in the septum to prevent possible pressure build-up in the system.
IT IS IMPORTANT THAT NO LOSS OF REACTANTS OCCURS DURING REFLUXING. THEREFORE, WATCH YOUR REACTION MIXTURE CAREFULLY AND DO NOT ALLOW THE REFLUXING VAPORS TO RISE ABOVE THE LOWER HALF OF YOUR REACTION TUBE. Reflux gently for at least one hour. Cool the reaction mixture and transfer it to a centrifuge tube which contains 1.5 mL water. Carefully rinse your reaction tube twice with 1-mL portions of dichloromethane (methylene chloride), and add these rinsings to the centrifuge tube.

(a) Extraction of the acid and ester into dichloromethane:

Cork the centrifuge tube and gently shake the contents. Allow the tube to stand until the layers separate and then use a Pasteur pipet to draw off the dichloromethane layer without removing any of the aqueous layer. Place the dichloromethane layer in a clean 10 mL Erlenmeyer flask or 20 mL vial. Carefully extract the aqueous layer remaining in the centrifuge tube again with 0.50 mL dichloromethane. After shaking, remove the dichloromethane layer and add it to your first dichloromethane extract contained in the flask or vial. Empty the aqueous layer in the centrifuge tube into a beaker and set aside. (This will eventually be discarded, but it is best not to throw out any layer in a liquid/liquid extraction until it is completed.)

(b) Extraction of 3-toluic acid into aqueous base:

Clean the centrifuge tube by rinsing with water, then acetone, and then water. Shake the excess water out of the centrifuge tube and pour the combined dichloromethane extracts from your flask or vial into it. Rinse the flask or vial with 0.5 mL of dichloromethane and add to the centrifuge tube. Now add 1.0 mL of 1M (5%) aqueous sodium hydroxide to the centrifuge tube, shake the mixture thoroughly, allow the layers to separate, draw off the NaOH layer using a clean Pasteur pipet, and place the NaOH layer in a reaction tube. Wash the dichloromethane in the centrifuge tube with 0.15 mL of water and add these washings to the NaOH solution contained in the reaction tube. Set the centrifuge tube containing the ester/dichloromethane solution aside. (This will eventually be discarded, but it is best not to throw out any layer in a liquid/liquid extraction until the experiment is completed.)

(c) Precipitation of the 3-toluic acid, extraction into dichloromethane, isolation and weighing:

Very carefully, with stirring, add dropwise just enough concentrated HCl to the contents of the reaction tube containing the 1M sodium hydroxide extracts to neutralize and to affect complete precipitation of 3-toluic acid.

Now, add 1.0 mL of dichloromethane, cork the reaction tube, and shake the contents gently but thoroughly. Allow the layers to separate, draw off the lower dichloromethane layer and transfer it to a 10-mL Erlenmeyer flask. Re-extract the aqueous layer in the reaction tube with another 1.0-mL portion of dichloromethane and transfer this dichloromethane layer into the flask with the previous dichloromethane extract. Dry the combined dichloromethane extracts (approximately 2 mL) with anhydrous Na₂SO₄ and transfer the dichloromethane to a tared test tube. Wash the residual Na₂SO₄ with approximately 0.5 mL of dichloromethane and add the washing to the contents of the tared test tube. Using a sand bath and boiling stick, IN THE HOOD, evaporate the solvent and determine the mass of the residual 3-toluic acid.

Analysis:

In addition to TLC analysis, you may be instructed to analyze your final product by IR or NMR. Analyze your sample according to your assignment sheet and the instructions on Sample Preparation in the Lab Guide.

Final Report

Using the mass of the unreacted 3-toluic acid and the original masses of the reactants, determine the equilibrium amounts of reactants and products and calculate Kₑq for this esterification reaction. Note that the equilibrium expression involves molarity terms. Although the volume of the equilibrium reaction mixture is
unknown, in this particular experiment it is not necessary to know the volume because the volume terms cancel out in the expression for $K_{eq}$. Show clearly your method of calculation for each equilibrium quantity and for the equilibrium constant.

Postlab Questions
1. Explain how using wet methanol would change the outcome of this experiment.
2. Compare and explain the solubilities of 3-toluic acid and sodium 3-methyl benzoate in water and dichloromethane.
3. Describe another way that the equilibrium constant for the formation of methyl 3-methylbenzoate could be determined by a spectroscopic technique.
4. Assuming the procedure is followed correctly, what is the most significant source of error in the data used to calculate the equilibrium constant?

Sample Data and Calculations- Experiment 90

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Initial amount</th>
<th>Initial amount (moles)</th>
<th>Final amount</th>
<th>Final amount (moles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-toluic acid</td>
<td>0.280 g</td>
<td>0.00206</td>
<td>0.097 g</td>
<td>0.000713</td>
</tr>
<tr>
<td>methanol</td>
<td>0.63 mL</td>
<td>0.0155</td>
<td></td>
<td>0.0142</td>
</tr>
<tr>
<td>water</td>
<td>0</td>
<td>0</td>
<td></td>
<td>0.00135</td>
</tr>
<tr>
<td>methyl toluate</td>
<td>0</td>
<td>0</td>
<td></td>
<td>0.00135</td>
</tr>
</tbody>
</table>

Explanation:
0.097 g of 3-toluic acid was recovered (0.000713 mol), so $[0.00206 \text{ mol} - 0.000713 \text{ mol}] = 0.00135 \text{ mol}$ converted to the ester; in so doing, an equimolar amount of water was produced; the same amount of methanol was consumed, or $[0.0155-0.00135] = 0.0142 \text{ mol}$ of methanol.

$$K_{eq} = \frac{[\text{ester}] [\text{water}]}{[\text{mol ester}][\text{mol water}]} = \frac{[0.00135][0.00135]}{[0.000713][0.0142]} = 0.18$$