Carboxylic Acids Reactions and Derivatives

Materials

Medium test tubes (6)  Test tube rack  Beakers (50, 150, 400 mL)
Ice  Hot plate  Graduated cylinders (10, 25-mL)

Chemicals

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoic acid</td>
<td>10% NaOH</td>
</tr>
<tr>
<td>Methanol</td>
<td>conc. H$_2$SO$_4$</td>
</tr>
<tr>
<td>Ethylamine</td>
<td>Acetyl chloride</td>
</tr>
<tr>
<td>Sodium acetate</td>
<td>Red/Blue litmus papers</td>
</tr>
<tr>
<td>Acetamide</td>
<td>pH papers</td>
</tr>
<tr>
<td>10% H$_2$SO$_4$</td>
<td>Salicylic acid</td>
</tr>
</tbody>
</table>

Purpose – Study the Carboxylic acids and their derivatives with one or more carbonyl groups. Reactions such as formation and hydrolysis of carboxylic salts and esterification. This experiment will illustrate some of the more important reactions of carboxylic acids and their derivatives.

Introduction

Carboxylic acids contain one or more carboxyl functional groups (-COOH). The IUPAC nomenclature drops the ( -e ) of the suffix of the Alkane name and adds ( -oic acid), review the names of the first ten alkanes and convert these names to the corresponding carboxylic acid. The carboxyl functional group is polar, both at the carbonyl part and at the hydroxyl part because of the difference in electronegativity value of carbon - oxygen, and oxygen - hydrogen. Thus carboxylic acids form hydrogen bond with themselves and any other appropriate polar molecule, and this structure will influence their physical properties and their chemical properties as we have seen in other cases. Note that if the number of total carbons is more than one, for example six, then five of the carbons are hydrocarbons and non-polar. The resulting molecule then has a hydrophilic part (the carboxyl group) and a hydrophobic part (the other five carbons with their associated hydrogen atoms). One area will be soluble in water and the other not soluble in water. Note also that the hydrocarbon part has much reduced carbon. The carboxyl group differs from a hydroxyl group in having a delocalized negative charge and this results in resonance stability. Note this means that either oxygen (carbonyl or hydroxyl) can double bond when proton is removed from hydroxyl.

Carboxylic acids are an important class of organic compounds. Other important classes of compounds called acid derivatives are related to acids but differ from them in that the hydroxyl portion of the carboxyl function is replaced by other groups. Among these acid derivatives are the acyl halides, anhydrides, esters, and amides.

\[
\begin{align*}
\text{O} && \text{O} && \text{O} && \text{O} \\
R - C - X && R - C - O - C - R && R - C - O - R && R - C - NH_2 \\
\text{acyl halide} && \text{acid anhydride} && \text{ester} && \text{amide}
\end{align*}
\]
Review carboxylic acid derivatives nomenclature

**Acyl Halides:** The acyl group is named first, followed by the halogen name as a separate word.

\[ \text{CH}_3\text{CH}_2\text{COCl} \] is propanoyl chloride (or propionyl chloride).

**Acid anhydrides:** The name of the related acid(s) is used first, followed by the separate word "anhydride".

\[ (\text{CH}_3(\text{CH}_2)_2\text{CO})_2\text{O} \] is butanoic anhydride

\[ \text{CH}_3\text{COO}\text{COCH}_2\text{CH}_3 \] is ethanoic propanoic anhydride (or acetic propionic anhydride).

**Esters:** The alkyl group is named first, followed by a derived name for the acyl group, the oic or ic suffix in the acid name is replaced by ate.

\[ \text{CH}_3(\text{CH}_2)_2\text{CO}_2\text{C}_2\text{H}_5 \] is ethyl butanoate (or ethyl butyrate)( ethylpropyl ester).

Cyclic esters are called lactones. A Greek letter identifies the location of the alkyl oxygen relative to the carboxyl carbonyl group.

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{O} \\
\end{array}
\]

4-butanolide (butanolactone)

**Amides:** The name of the related acid is used first and the oic acid or ic acid suffix is replaced by amide (only for 1º-amides).

\[ \text{CH}_3\text{CONH}_2 \] is ethanamide (or acetamide)(1º amide)

2º & 3º-amides have alkyl substituents on the nitrogen atom. These are designated by "N-alkyl" term(s) at the beginning of the name.

\[ \text{CH}_3(\text{CH}_2)_2\text{CONHC}_2\text{H}_5 \] is N-ethylbutanamide; (2º amide)

\[ \text{HCON(CH}_3)_2 \] is N,N-dimethylmethanamide (or N,N- dimethylformamide) (3º amide).

Cyclic amides are called lactams. A Greek letter identifies the location of the nitrogen on the alkyl chain relative to the carboxyl carbonyl group.

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{N- H} \\
\end{array}
\]

butanolactam
PART A. Carboxylic Acid Salts

I. Salt Formation

Carboxylic acids may be neutralized by strong base to give salts. Because salts are ionic and usually water-soluble, acids that are only slightly soluble in water can be extracted by aqueous base from a solution in an organic solvent.

\[
\begin{align*}
\text{R - C - OH} & \quad + \quad \text{NaOH} \\
\rightarrow & \\
\text{R - C - O - Na}^+ & \quad + \quad \text{H}_2\text{O}
\end{align*}
\]

sodium salt (water soluble)

**Example:**

\[
\begin{align*}
\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{C} - \text{OH} & \quad + \quad \text{NaOH} \\
\rightarrow & \\
\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{C} - \text{O} - \text{Na}^+ & \quad + \quad \text{H}_2\text{O}
\end{align*}
\]

Butanoic acid

sodium butanoate salt

II. Salt Hydrolysis

Because carboxylic acids are weak acids partially dissociated in aqueous solution, their salt solutions are alkaline. In water, a carboxylic acid salt hydrolyzes to the undissociated acid and hydroxide ion.

\[
\begin{align*}
\text{R - C - O - Na}^+ & \quad + \quad \text{H}_2\text{O} \\
\rightarrow & \\
\text{R - C - OH} & \quad + \quad \text{NaOH}
\end{align*}
\]

sodium salt (water soluble)

**Example:**

\[
\begin{align*}
\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{C} - \text{O} - \text{Na}^+ & \quad + \quad \text{H}_2\text{O} \\
\rightarrow & \\
\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{C} - \text{OH} & \quad + \quad \text{NaOH}
\end{align*}
\]

Butanoic acid

sodium butanoate salt
PART B. Esters:

Esters can be prepared by the reaction of alcohols with carboxylic acids or their derivatives. The acid catalyzed reaction of an alcohol with a carboxylic acid is most commonly used for such preparations. The acyl halide ion is a good leaving group making acyl halides very reactive toward nucleophilic acyl substitution. Acid halides (or acyl halides) are highly reactive that they are not found in nature, since they even react with water. For small-scale preparations, however, the reaction of an acyl halide with an alcohol is often faster and simpler.

\[
\text{R - C - OH} + \text{R}'\text{-OH} \xrightleftharpoons{\text{H}^+} \text{R - C - OR'} + \text{H}_2\text{O}
\]

\[
\text{R - C - O-X} + \text{R}'\text{-OH} \xrightleftharpoons{\text{H}^+} \text{R - C - O - R'} + \text{HX}
\]

Example:

\[
\text{\begin{array}{c}
\text{C - OH} \\
\text{CH}_3\text{-OH} \\
\text{C - O Cl}
\end{array}} \xrightleftharpoons{\text{H}^+} \text{\begin{array}{c}
\text{C - O - CH}_3 \\
\text{} \\
\text{C - O - CH}_3
\end{array}}
\]

PART C. Amides: Hydrolysis of an Amide

Three classes of amides are known:

\[
\text{R - C - NH}_2 \quad \text{R - C - NH - R'} \quad \text{R - C - N - R'' - R'}
\]

Primary ($1^\circ$) amide secondary ($2^\circ$) amide tertiary ($3^\circ$) amide

Benzamide N – methylbenzamide N – ethyl – N – methylbenzamide
Of the various acid derivatives studied here, amides are the least reactive toward nucleophilic attack, because the unshared electron pair on the nitrogen is delocalized to the carbonyl carbon through resonance.
Thus, unlike most acyl halides or anhydrides, amides must be heated to boiling with aqueous acid or base in order to hydrolyze them. For a primary amide, the product will be ammonium ion and the acid (for acidic hydrolysis) or ammonia and carboxylate ion (for alkaline hydrolysis). The reaction mechanisms are similar to those for the hydrolysis of other acid derivatives.

In this experiment you will hydrolyze acetamide under alkaline and acidic conditions.

In basic solution:

\[
\begin{align*}
  \text{R - C - NH}_2 + \text{H}_2\text{O} + \text{OH}^- & \rightarrow \text{R - C - O}^- + \text{NH}_3(\text{g}) \\
\end{align*}
\]

In acidic solution:

\[
\begin{align*}
  \text{R - C - NH}_2 + \text{H}_2\text{O} + \text{H}^+ & \rightarrow \text{R - C - O}^- \text{H} + \text{NH}_4^+ \\
\end{align*}
\]

Ammonium carboxylate ion

Example:
Safety Note

Caution:
1. Acetic anhydride is irritating in the liquid or vapor state. Avoid contact with skin and eyes.
2. When handling concentrated sulfuric or phosphoric acid be careful to avoid contact with skin and clothing. Wear disposable gloves.

Procedure

Part A- Carboxylic Acid Salts.

I. Salt Formation

In each of two test tubes, place 0.1 g of benzoic acid. To one tube, add 3 ml of cold water, to the other, add 3 ml of 10% sodium hydroxide solution. Shake both tubes, observe, record the result, and write a complete reaction.

II. Salt Hydrolysis

This hydrolysis can be demonstrated by testing the salt solution with litmus paper. Dissolve approximately 0.2 g of sodium acetate in 5 ml of distilled water. Test the resulting solution with litmus paper, and note the results. Wash the aqueous solution down the sink with plenty of water. Record the result, and write a complete reaction.

PART B. Esters - Preparation of Methyl Salicylate (Oil of Wintergreen)

I. Dissolve 0.5 g of salicylic acid in 5 ml of methanol in a small beaker. Cautiously, and with constant stirring, add 10 drops of concentrated sulfuric acid to the mixture. Heat the mixture on the steam bath for 10 min, then pour it over about 10 g of ice in a small beaker. Stir well and cautiously observe the odor of the product by gently wafting the vapors toward your nose. Record the result, and write a complete reaction.

II. Add drop-by-drop 1 ml (~ 20 drops) of acetyl chloride to 1 ml of butanol. Allow to stand for about 2 minutes and then pour carefully into 5 ml of water (acetyl chloride reacts vigorously with water). Note the odor of solution by wafting the smell toward your nose. Remove a little of the insoluble layer with a dropper and test its solubility in 5% NaOH solution.

PART C. Amides: Hydrolysis of an Amide

Add 0.5 g of acetamide to 5 ml of 10% sodium hydroxide solution in a test tube, and gently warm the solution, and heat the mixture to boiling. Note the odor of the evolved gas by gently wafting its vapors toward your nose. Test the gas by holding a piece of moist red litmus paper in the mouth of the tube. Repeat the experiment with 0.5 g of acetamide and 5 ml of 10% sulfuric acid. Record the result, and write a complete reaction(s).
EXPERIMENT 8 (Organic Chemistry II)

Carboxylic Acids Reactions and Derivatives

REPORT FORM

Name _________________________________
Instructor ___________________________
Date _______________

Part A- Carboxylic Acid Salts.

I. Salt Formation

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Solubility(observation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoic acid</td>
<td>Cold water</td>
<td>.......................</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>10% NaOH</td>
<td>.......................</td>
</tr>
</tbody>
</table>

Reaction: ________________________________________________________________________________

II. Salt Hydrolysis

Sodium acetate solution changed the color of litmus from ________ to _________ .

Reaction: ________________________________________________________________________________

PART B. Esters - Preparation of Methyl Salicylate (Oil of Wintergreen)

I. Describe the odor of the product. _________________________________________________________

Reaction: ________________________________________________________________________________

II. Describe the odor of the product. _________________________________________________________

Reaction: ________________________________________________________________________________

PART C. Amides - Hydrolysis of an Amide

a. Odor of the gas and its effect on litmus for basic hydrolysis: ________________________________

Reaction: ________________________________________________________________________________

b. Odor of the gas and its effect on litmus for acidic hydrolysis: ________________________________

Reaction: ________________________________________________________________________________
1. Write a complete reaction of succinic acid and acetic anhydride.

2. Write an equation that accounts for the solubility of propanoic acid in aqueous base.

3. Write equations that describe the reaction mechanism for acid hydrolysis of each of the following compounds.
   a) Acetyl Chloride  
   b) Acetic anhydride

4. Explain why acetyl chloride is hydrolyzed faster than benzoyl chloride.

5. Write an equation for the reaction of n-butyl alcohol with acetyl chloride. What gas evolved?
1. Write an equation for the reaction of aniline with acetic anhydride.

2. Give structure for the following compounds;
   a) pentanolactam    b) pentanolactone

3. Name two dicarboxylic acids and draw their structures.

4. What is the difference between dehydration and hydrolysis? Give examples.

5. Define esterification and give an example.