Carboxylic Acids and their Derivatives

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Carboxylic acids are a group of compounds containing the functional group -COOH. They represent a large class of organic compounds, with varying applications from numerous natural products to synthetic drugs and hormones. In this article, the carboxylic acid family of compounds will be given focus. Covered in this article is the simple nomenclature and reactivity of these compounds. How the compounds participate in nucleophilic substitution reactions and how the different carboxylic acid derivatives are formed.

Carboxylic Acid

General formula:

\[
\begin{align*}
\text{R}\text{C} &= \text{O} \\
\text{OH}
\end{align*}
\]

Nomenclature: The name is given by replacing the -e at the end of the corresponding alkane name with -oic acid.

Carboxylic acids, RCOOH, are one of the most commonly encountered organic compounds. The reactivities of carboxylic acids are the -COOH functional group, specifically due to the inherent polarity of the carbonyl (C=O) group. The most electron-
rich site for the compound is the carbonyl oxygen, while the most electron-poor site is the hydrogen atom attached to the OH group. Because of this, the compound is relatively polar.

The -COOH functional group also affects the physical properties of the compound. Carboxylic acids have relatively higher boiling and melting points, compared to hydrocarbons and other oxygen-containing organic compounds of similar size and shape.

The main factor for their differences in their physical properties is the possibility of hydrogen bonding through two oxygen atoms in the structure of carboxylic acid. The two oxygen atoms are tightly held by hydrogen bonds, making the compound harder to convert from one state to another.

Carboxylic acids are considered weak acids as they can donate an H⁺ to a small extent. When a proton is eliminated from the OH group of the compound, the electrons in the remaining –COO– group exhibit resonance, causing a slight stabilization of the resulting anion.

Replacing the –OH group in the structure of carboxylic acid leads to the formation of different carboxylic acid derivatives. Replacing the OH group with a halide group (-X) leads to a formation of acyl chlorides. Replacing the OH group with an amino group (-NH₂) leads to a formation of amides. Replacing the OH group with an -OR leads to a formation of esters. Replacing the OH group with a –OOCR leads to the formation of acid anhydrides and much more. Below are some examples of these carboxylic acid derivatives.

![Structure of Carboxylic acid and its derivatives](image)

Nomenclature

The simple way of naming carboxylic acids is by counting the number of carbons in the longest continuous chains that include the carboxyl carbon. The ‘e’ in the alkane or alkene name corresponding to that number of carbon is then replaced with -oic acid. The table below shows some of the common carboxylic acids with their systematic names.

**Table 1: Examples of carboxylic acids and their systematic names**
In most of the examples above, the only prominent functional group is the carboxylic acid group. However, it is also possible to have a carboxylic acid with one or more other functional groups present in the chain. For example, hydroxyethanoic acid would mean an ethanoic acid with another hydroxy group. In naming organic compounds, the functional group given the highest priority is the carboxylic acid group. The carbon where the other functional groups are attached is assigned numbers with the carbonyl carbon of the carboxylic acid group assigned as the carbon 1. In writing their name, the substituents are arranged in alphabetical order, regardless of their carbon number. Below are some of the examples of mono and di-substituted carboxylic acid.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Alkane name</th>
<th>Systematic name</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>methane</td>
<td>Methanoic acid</td>
</tr>
<tr>
<td></td>
<td>ethane</td>
<td>Ethanoic acid</td>
</tr>
<tr>
<td></td>
<td>propene</td>
<td>Propenoic acid</td>
</tr>
<tr>
<td></td>
<td>propyne</td>
<td>Propynoic acid</td>
</tr>
<tr>
<td></td>
<td>benzene</td>
<td>Benzoic acid</td>
</tr>
</tbody>
</table>

Table 2: Examples of carboxylic acids with other substituents in the chain

<table>
<thead>
<tr>
<th>Structure</th>
<th>IUPAC Name</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2-hydroxypropanoic acid</td>
</tr>
<tr>
<td></td>
<td>4-amino-2-chlorobutanoic acid</td>
</tr>
<tr>
<td></td>
<td>3-oxopropanoic acid</td>
</tr>
</tbody>
</table>

In cases where the compound has two carboxylic acid groups on both sides of the longest carbon chain, the suffix -dioic acid is added to the alkane name for the longest carbon chain. Below is the structure of butanedioic acid:
Nucleophilic Acyl Substitution

*Because of the inherent polarity of the carbonyl C=O bond, carboxylic acids are prone to attack via nucleophilic substitution reaction.* Just like in aldehyde, the nucleophile attacks the carbonyl carbon, forming a tetrahedral intermediate and, in the process, producing different possible carboxylic acid derivatives. In a nucleophilic acyl substitution reaction, when the nucleophile attaches itself to the carbon atom, the next step involves elimination of one of the two substituents attached to the carbonyl carbon.

Unlike in aldehydes and ketones where an H or other alkyl substituents are attached to the carbonyl carbon, in a carboxylic acid, one of the substituents in a carboxylic acid or its derivatives is a good leaving group compared to the H or an alkyl substituent. Since the H and alkyl groups in aldehyde or ketones are not good leaving groups, they undergo nucleophilic addition, while for carboxylic acids it is nucleophilic substitution reaction. The general mechanism for this type of reaction is shown in the figure:

Reactivity of Carboxylic Acid Derivatives

The reaction only involves two steps. Both of these steps are important in predicting the reactivity of the compound. Electronic and steric factors are important to consider in comparing reactivities of carboxylic acids and their derivatives.

Steric factors are to be considered because the presence of bulky groups significantly affects the rate of the first step. The bulkier the alkyl group attached to the carbonyl carbon, the harder it is for the nucleophile to attack the carbonyl carbon.

The polarization of acyl compounds is also important in predicting the reactivities of the compounds. More strongly polarized acyl compounds react more readily than polar ones. This means acyl chlorides will react faster in a nucleophilic substitution, compared to the
Hydrolysis

When carboxylic acid derivatives are reacted with water, all reactions lead to a production of carboxylic acids. This is because groups like \(-\text{NH}_2\) and \(-\text{Cl}\), for example, are better-leaving groups compared to an-\(\text{OH}\). So, when the water molecule attaches itself to the carbonyl carbon, the leaving groups are readily eliminated together with a proton from the water. Below is the mechanism for the hydrolysis reaction of acyl chloride. The same mechanism is followed by the other carboxylic acid derivatives.

![Mechanism of the hydrolysis of acyl chloride](image)

Amides Formation from Esters

An **aminolysis** reaction is possible for esters using ammonia or amines as nucleophiles. However, this reaction is not commonly employed, as the use of acyl halides lead to faster reactions.

Review Questions

The correct answers can be found below the references.

1. **What are the products of the reaction below?**

   A. \(\text{H}_3\text{C}---\text{OH}\) only
   
   B. \(\text{H}_3\text{C}---\text{OH}\) only
2. **What is the reason why carboxylic acids have higher boiling points compared to an alcohol of similar molecular weight?**

   A. Both exhibit London Dispersion Forces.
   B. The –COOH group is more polar compared to the –OH group.
   C. Carboxylic acids exhibit hydrogen bonding while alcohols don’t.
   D. Carboxylic acids can form H-bonds with the two oxygen atoms, while the alcohol can only form through its sole oxygen atom.

References


**Correct answers:** 1C, 2D

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