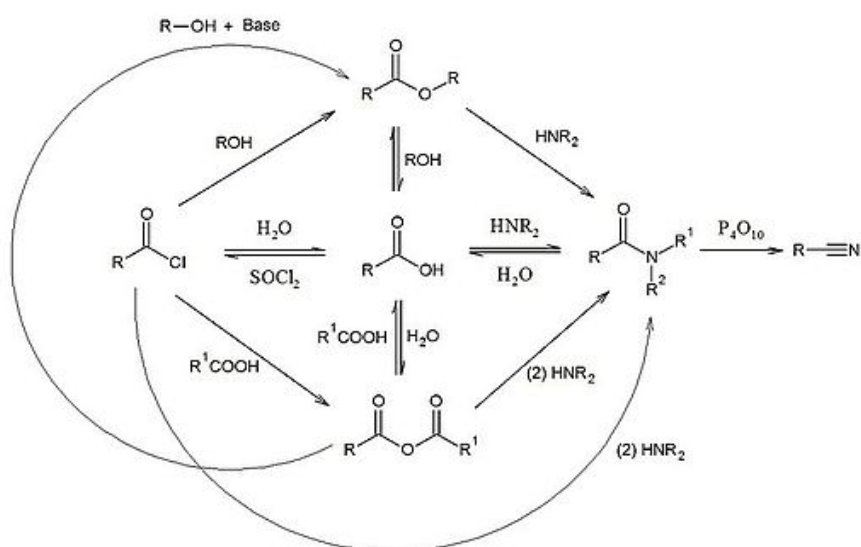


## Carboxylic Acids and their Derivatives

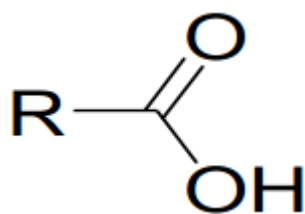
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Carboxylic acids are a group of compounds containing the functional group  $\text{-COOH}$  and represent a large class of organic compounds with varying applications from numerous natural products to synthetic drugs and hormones. This article provides a review of the simple nomenclature and reactivity of carboxylic acids, as well as their participation in nucleophilic substitution reactions and the formation of carboxylic acid derivatives.



### Carboxylic Acid

**General formula:**



**Nomenclature:** In the naming of carboxylic acids, the  $\text{-e}$  at the end of the corresponding alkane is replaced with  $\text{-oic acid}$ . Carboxylic acids,  $\text{RCOOH}$ , are one of the most commonly encountered organic compounds. The reactivities of carboxylic acids are centered around the  $\text{-COOH}$  functional group, specifically due to the inherent polarity of the carbonyl ( $\text{C=O}$ ) group contained within it. 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  $\text{OH}$  group, resulting in the relative polarity of the compound. The

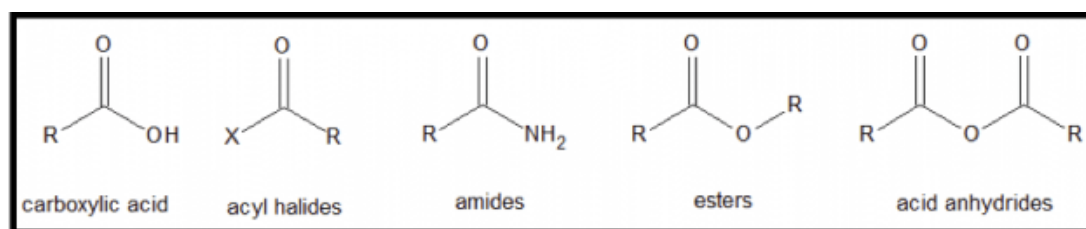
-COOH functional group also affects the physical properties of the compound. Carboxylic acids have relatively higher boiling and melting points compared to hydrocarbons and other oxygen-containing organic compounds of similar size and shape. The main factor contributing to the differences in the physical properties of carboxylic acids is the possibility of hydrogen bonding through two oxygen atoms present within its structure. The 2 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 a proton ( $H^+$ ), 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.

Common replacements of the -OH group:

- 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 the formation of acyl chlorides.
- Replacing the -OH group with an amino group (-NH<sub>2</sub>) leads to the formation of amides.
- Replacing the -OH group with an -OR leads to the 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.

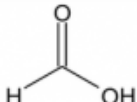
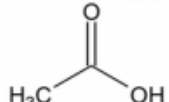
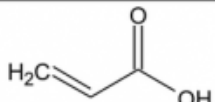
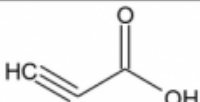
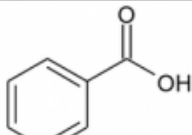


"Structure of Carboxylic acid and its derivatives" by Mark Xavier Bailon

## Nomenclature

The simple way of naming carboxylic acids is by counting the number of carbons in the longest continuous chain that includes the carboxyl carbon. The -e in the alkane or alkene name corresponding to the identified number of carbons 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**

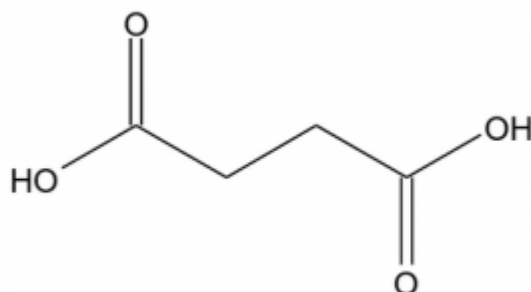
Structure	Alkane name	Systematic name
	methane	<b>Methanoic acid</b>
	ethane	<b>Ethanoic acid</b>
	propene	<b>Propenoic acid</b>
	propyne	<b>Propynoic acid</b>
	benzene	<b>Benzoic acid</b>

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 names, 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.

In cases where the compound has 2 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:

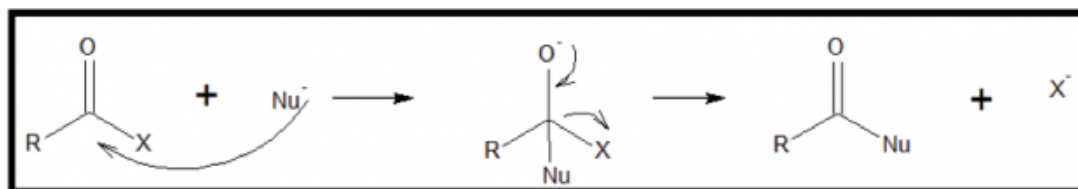


"Butanedioic Acid" by Mark Xavier Bailon

## 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 aldehydes, 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, elimination of one of the 2 substituents attached to the carbonyl carbon takes place as the nucleophile attaches itself to that carbon atom.

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



"Mechanism of Nucleophilic Acyl Substitution Reactions" by Mark Xavier Bailon

## Reactivity of Carboxylic Acid Derivatives

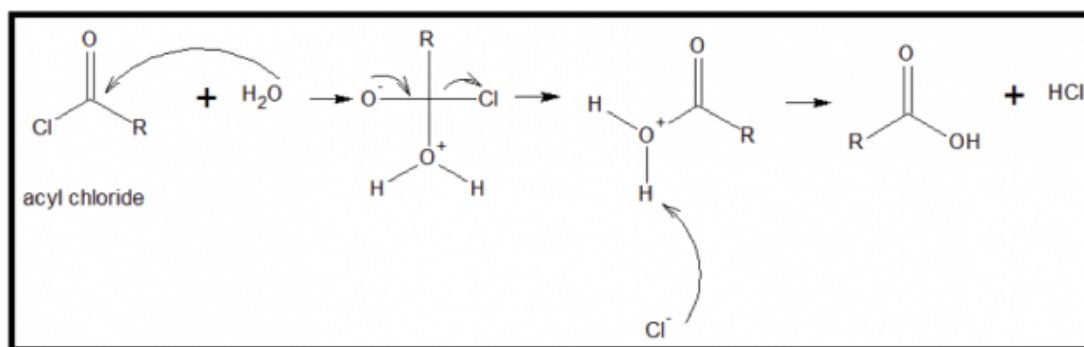
The production of carboxylic acid derivatives is a two-step reaction, each of which is important in predicting the reactivity of the compound. Furthermore, electronic and steric factors are also important to consider when comparing reactivities of carboxylic acids and their derivatives.

Steric factors are an important consideration for assessing reactivity because the presence of bulky groups significantly affects the rate of the first step in derivative production; 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. More strongly polarized acyl compounds react more readily than less polar ones. This means, for example, acyl chlorides will react faster in nucleophilic substitution compared to the less polarized amides.

## Hydrolysis

When carboxylic acid derivatives react with water, all reactions lead to a production of carboxylic acids. This is because groups like -NH<sub>2</sub> and -Cl, for example, are better-leaving groups compared to -OH. Therefore, when the water molecule attaches itself to the carbonyl carbon, the leaving groups are readily eliminated together with an H<sup>+</sup> from the water. Below is the mechanism for the hydrolysis of acyl chloride. The same mechanism is followed by other carboxylic acid derivatives.



"Mechanism of the hydrolysis of acyl chloride" by Mark Xavier Bailon

## 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.

## References

McMurry, J. (2008). Organic Chemistry. 7th ed. USA. Brooks/Cole, Thomson Learning Inc.

Carey, F. (2000). Organic Chemistry. 4th ed. USA. McGraw-Hill Companies, Inc.

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