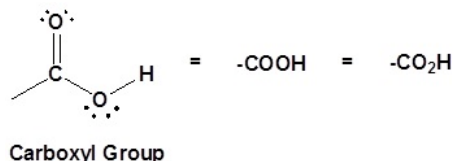


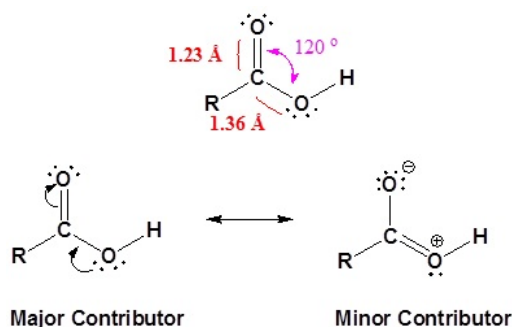
21.1: STRUCTURE AND PROPERTIES OF CARBOXYLIC ACIDS AND THEIR SALTS

STRUCTURE OF THE CARBOXYL ACID GROUP

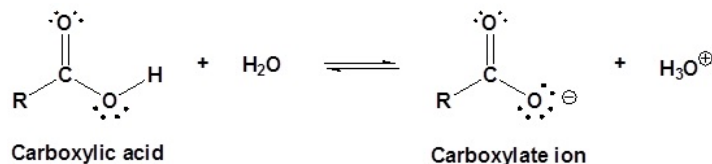
Carboxylic acids are organic compounds which incorporate a carboxyl functional group, CO_2H . The name carboxyl comes from the fact that a carbonyl and a hydroxyl group are attached to the same carbon.



The carbon and oxygen in the carbonyl are both sp^2 hybridized which give a carbonyl group a basic trigonal shape. The hydroxyl oxygen is also sp^2 hybridized which allows one of its lone pair electrons to conjugate with the pi system of the carbonyl group. This makes the carboxyl group planar and can be represented with the following resonance structure.



Carboxylic acids are named such because they can donate a hydrogen to produce a carboxylate ion. The factors which affect the acidity of carboxylic acids are discussed in the next section of this chapter.



PHYSICAL PROPERTIES OF SOME CARBOXYLIC ACIDS

Formula	Common Name	Source	IUPAC Name	Melting Point	Boiling Point
HCO_2H	formic acid	ants (L. formica)	methanoic acid	8.4 °C	101 °C
$\text{CH}_3\text{CO}_2\text{H}$	acetic acid	vinegar (L. acetum)	ethanoic acid	16.6 °C	118 °C
$\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$	propionic acid	milk (Gk. protus prion)	propanoic acid	-20.8 °C	141 °C
$\text{CH}_3(\text{CH}_2)_2\text{CO}_2\text{H}$	butyric acid	butter (L. butyrum)	butanoic acid	-5.5 °C	164 °C
$\text{CH}_3(\text{CH}_2)_3\text{CO}_2\text{H}$	valeric acid	valerian root	pentanoic acid	-34.5 °C	186 °C
$\text{CH}_3(\text{CH}_2)_4\text{CO}_2\text{H}$	caproic acid	goats (L. caper)	hexanoic acid	-4.0 °C	205 °C
$\text{CH}_3(\text{CH}_2)_5\text{CO}_2\text{H}$	enanthic acid	vines (Gk. oenanthe)	heptanoic acid	-7.5 °C	223 °C
$\text{CH}_3(\text{CH}_2)_6\text{CO}_2\text{H}$	caprylic acid	goats (L. caper)	octanoic acid	16.3 °C	239 °C
$\text{CH}_3(\text{CH}_2)_7\text{CO}_2\text{H}$	pelargonic acid	pelargonium (an herb)	nonanoic acid	12.0 °C	253 °C
$\text{CH}_3(\text{CH}_2)_8\text{CO}_2\text{H}$	capric acid	goats (L. caper)	decanoic acid	31.0 °C	219 °C

Saturated			Unsaturated		
Formula	Common Name	Melting Point	Formula	Common Name	Melting Point
$\text{CH}_3(\text{CH}_2)_{10}\text{CO}_2\text{H}$	lauric acid	45 °C	$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_4\text{CO}_2\text{H}$	palmitoleic acid	0 °C
$\text{CH}_3(\text{CH}_2)_{12}\text{CO}_2\text{H}$	myristic acid	55 °C	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_4\text{CO}_2\text{H}$	oleic acid	13 °C
$\text{CH}_3(\text{CH}_2)_{14}\text{CO}_2\text{H}$	palmitic acid	63 °C	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_3\text{CO}_2\text{H}$	linoleic acid	-5 °C
$\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$	stearic acid	69 °C	$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{CO}_2\text{H}$	linolenic acid	-11 °C
$\text{CH}_3(\text{CH}_2)_{18}\text{CO}_2\text{H}$	arachidic acid	76 °C	$\text{CH}_3(\text{CH}_2)_4(\text{CH}=\text{CHCH}_2)_4(\text{CH}_2)_2\text{CO}_2\text{H}$	arachidonic acid	-49 °C

The table at the beginning of this page gave the melting and boiling points for a homologous group of carboxylic acids having from one to ten carbon atoms. The boiling points increased with size in a regular manner, but the melting points did not. Unbranched acids made up of an even number of carbon atoms have melting points higher than the odd numbered homologs having one more or one less carbon. This reflects differences in intermolecular attractive forces in the crystalline state. In the table of fatty acids we see that the presence of a cis-double bond significantly lowers the melting point of a compound. Thus, palmitoleic acid melts over 60° lower than palmitic acid, and similar decreases occur for the C₁₈ and C₂₀ compounds. Again, changes in crystal packing and intermolecular forces are responsible.

The factors that influence the relative boiling points and water solubilities of various types of compounds were discussed earlier. In general, dipolar attractive forces between molecules act to increase the boiling point of a given compound, with hydrogen bonds being an extreme example. Hydrogen bonding is also a major factor in the water solubility of covalent compounds. To refresh your understanding of these principles [Click Here](#). The following table lists a few examples of these properties for some similar sized polar compounds (the non-polar hydrocarbon hexane is provided for comparison).

The first five entries all have oxygen functional groups, and the relatively high boiling points of the first two is clearly due to hydrogen bonding. Carboxylic acids have exceptionally high boiling points, due in large part to dimeric associations involving two hydrogen bonds. A structural formula for the dimer of acetic acid is shown here. When the mouse pointer passes over the drawing, an electron cloud diagram will appear. The high boiling points of the amides and nitriles are due in large part to strong dipole attractions, supplemented in some cases by hydrogen bonding.

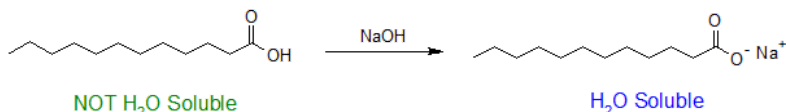


Physical Properties of Some Organic Compounds

Formula	IUPAC Name	Molecular Weight	Boiling Point	Water Solubility
CH ₃ (CH ₂) ₂ CO ₂ H	butanoic acid	88	164 °C	very soluble
CH ₃ (CH ₂) ₄ OH	1-pentanol	88	138 °C	slightly soluble
CH ₃ (CH ₂) ₃ CHO	pentanal	86	103 °C	slightly soluble
CH ₃ CO ₂ C ₂ H ₅	ethyl ethanoate	88	77 °C	moderately soluble
CH ₃ CH ₂ CO ₂ CH ₃	methyl propanoate	88	80 °C	slightly soluble
CH ₃ (CH ₂) ₂ CONH ₂	butanamide	87	216 °C	soluble
CH ₃ CON(CH ₃) ₂	N,N-dimethylethanamide	87	165 °C	very soluble
CH ₃ (CH ₂) ₄ NH ₂	1-aminobutane	87	103 °C	very soluble
CH ₃ (CH ₂) ₃ CN	pentanenitrile	83	140 °C	slightly soluble
CH ₃ (CH ₂) ₄ CH ₃	hexane	86	69 °C	insoluble

CARBOXYLATE SALTS

The water solubility of carboxylic acids is determined by the ratio of carboxyl groups to the the number of carbon atoms in the molecule following the "4 to 6 Rule". As seen with amines, water solubility of carboxylic acids can be increased when they are ionized. Typically a strong base is used to deprotonate the carboxylic acid and drive the reaction to completion as shown below.



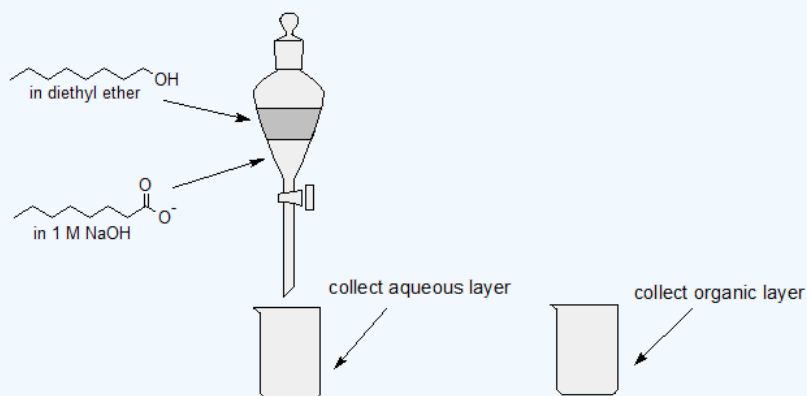
Exercise

1. Use acid-base chemistry and differences in water solubility to separate 1-octanol from octanoic acid using the following solutions: 1 M NaOH, ether, and 6 M HCl and any lab equipment.

Answer

- 1.

- Step 1: Dissolve both compounds in ether and add to a separatory funnel.
 Step 2: Add 1 M NaOH to the separatory funnel.
 Step 3: Mix well to deprotonate the carboxylic acid to a water soluble carboxylate ion.
 Step 4: Collect the aqueous and organic layers.



- Step 5: Acidify the aqueous layer using 6 M HCl to reprotonate the carboxylate to octanoic acid.
 Step 6: Isolate the octanoic acid by vacuum filtration and allow sample to dry.
 Step 7: Isolate the 1-octanol by removing the ether by evaporation using a warm water bath & a gentle flow of nitrogen gas.

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