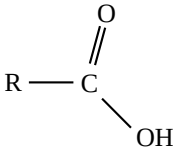
Carboxylic acid or alkanoic acids

These are cmpounds with the formula



where R is a hydrogen or an alkyl group.

The carboxylic group is a combination of carbonyl group abs an hydroxyl group(OH): the name carboxylic group.

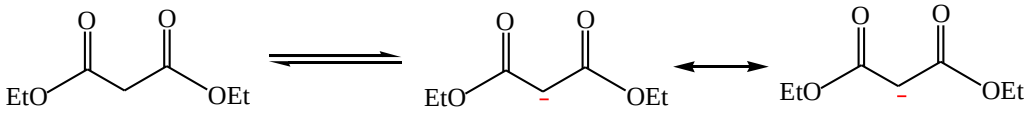
Nomenclature

1. Their names end with suffic “oic” followed by the word acid.
2. The carboxylic group must always be at the end of the chain and therefore it’s position need not to be specified. Take longest chain that contain the carboxylic group and start numbering from the carboxylic carbon

Examples	Systematic name	Common name
HCOOH	Mechanoic acid	Formic acid
CH_3COOH	Ethanoic	Acetic acid
CH_3CH_2COOH	Propanoic acid	Propionic acid
$CH_2CH_2CH_2COOH$	Butanoic acid	Butyric acid
$CH_3CH(CH_3)COOH$	2-methylpropanoic acid	Isobutyric acid

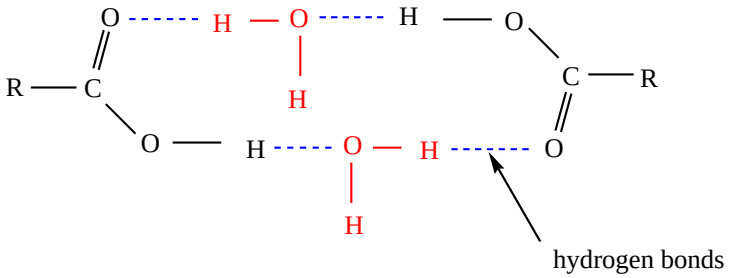
Physical properties

1. Lower member are liquids and higher members are waxy solids. With boiling points which are higher than expected, this because, their molecules are associated by hydrogen bonds.



$$RCH{=}CHR' \xrightarrow[\text{heat}]{\substack{1.\ KMnO_4,\ OH^- \\ 2.\ H_3O^+}} RCOOH + R'COOH$$

2. Lower members are soluble in water but the solubility decreases with the increasing molecular mass of carboxylic acid. This is because carboxylic acids are capable of formation of hydrogen bonds with water



3. Melting points

Compounds	Mpt (^{0}C)	Bpt (^{0}C)	Ka
HCOOH	8	100.5	1.7×10^{-4}
CH_3COOH	16.6	118	1.77×10^{-5}
CH_3CH_2COOH	21	141	1.34×10^{-5}
$CH_3(CH_2)_2COOH$	-6	164	1.54×10^{-5}
$CH_3(CH_2)_3COOH$	-34	187	1.52×10^{-5}
$CH_3(CH_2)_4COOH$	-3	205	
$CH_3(CH_2)_5COOH$	16	259	

Generally the melting point increase with the molecular mass. However, the melting points of lower carboxylic acids are relatively higher than those of higher carboxylic acids because they form strongerhydrogen bonds.

4. The acidity of carboxylic acids decrease with the increase in molecular mass due to positive inductive effect of alkyl group. Electron with drawing groups make carboxylic acid more acidic. For example CCl_3COOH is more acidic than CH_3COOH.

Methods of preparation

1. By oxidation of primary alcohols using $K_2Cr_2O_7/H^+$, $Na_2Cr_2O_7/H^+$, or $KMnO_4/H^+$

i.e $RCH_2OH \xrightarrow{[O]} RCHO \xrightarrow{[O]} RCOOH$

e.g. $CH_3CH_2OH \xrightarrow{K_2Cr_2O_7/H^+} CH_3CHO \xrightarrow{K_2Cr_2O_7/H^+} CH_3COOH$

2. Oxidation of aldehyde using $K_2Cr_2O_7/H^+$, $Na_2Cr_2O_7/H^+$, or $KMnO_4/H^+$

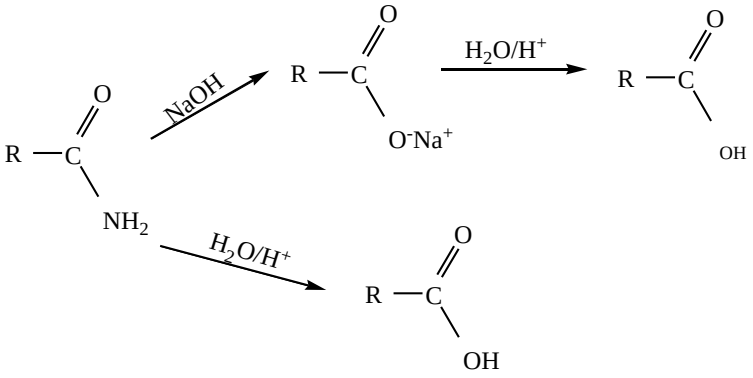
e.g. $CH_3CHO \xrightarrow{K_2Cr_2O_7/H^+} CH_3COOH$

3. Hydrolysis of nitrile in presence of a mineral acid.

i.e. $RCN \xrightarrow{H_2O,\ H^+} RCOOH$

e.g. $CH_3CH_2CHCH_3 \xrightarrow{H^+} CH_3CH_2CHCH_3$ (CN → COOH)

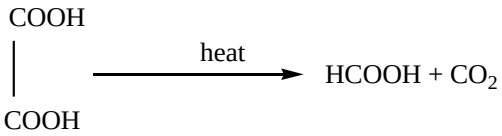
4. Hydrolysis of acid amide with a mineral acid or alkali



5. Reaction of carbon dioxide with a grignard reagent followed with hydrolysis.

$RMgX + CO_2 \xrightarrow{\text{dry ether}} RCO_2MgX \xrightarrow{\text{dry ether}} RCOOH$

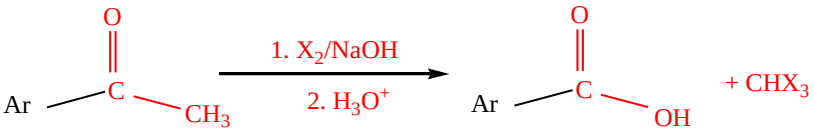
6. Preparation of methanoic acid
   By heating a solution of ethane dioic acid in propane-1,2,3-triol



7. Oxidation of alkenes using hot alkaline $KMnO_4$.

$RCH=CHR' \xrightarrow[\text{heat}]{\text{1. } KMnO_4,\ OH^-} RCOOH + R'COOH$ (2. H_3O^+)

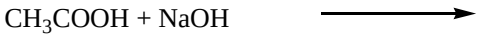
8. Oxidation of methyl ketone



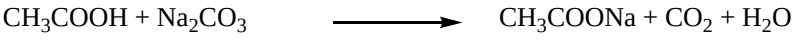
Chemical properties

1. Carboxylic acid react with base to form salts and even liberate caarbon dioxide from carbonates.

Examples



$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

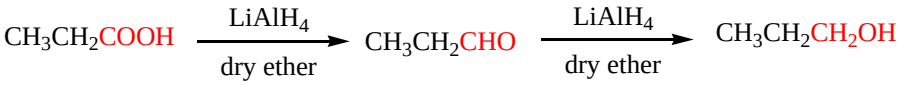


$$CH_3COOH + Na_2CO_3 \longrightarrow CH_3COONa + CO_2 + H_2O$$

2. Reduction of carboxylic acid

Carboxylic acids are resistant to reduction by mild reducing agents. However, can be reduced through aldehydes to primary alcohols by LiAlH4 in presence of dry ether.

Example

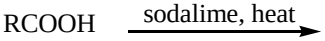


$$CH_3CH_2COOH \xrightarrow[\text{dry ether}]{LiAlH_4} CH_3CH_2CHO \xrightarrow[\text{dry ether}]{LiAlH_4} CH_3CH_2CH_2OH$$

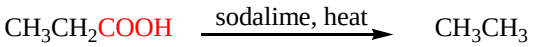
3. Decarboxylation

This is a reaction in which a molecule of CO2 is removed from carboxylic acids.

(i) Simple carboxylic acids are not easily decarboxylated but their salts are easily decarboxylated in presence of soda lime.



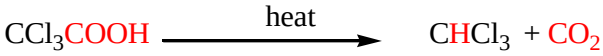
$$RCOOH \xrightarrow{\text{sodalime, heat}} RH$$

(ii) 

$$CH_3CH_2COOH \xrightarrow{\text{sodalime, heat}} CH_3CH_3$$

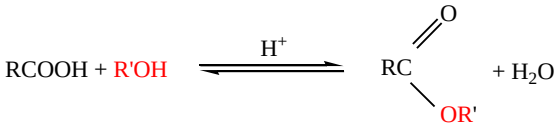
(iii) Acids with electron withdrawing groups on α-carbon are easily decarboxylated on heating.

Example



$$CCl_3COOH \xrightarrow{\text{heat}} CHCl_3 + CO_2$$

(iv) Esterification: Carboxylic acids react with alcohol in presence of mineral acids to form es



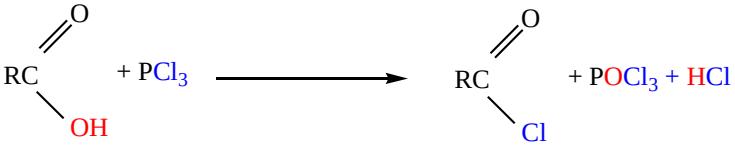
$$RCOOH + R'OH \underset{}{\overset{H^+}{\rightleftharpoons}} RC(=O)OR' + H_2O$$

Easter have got sweet smell; this is why this reaction is used in identification of carboxylic acids

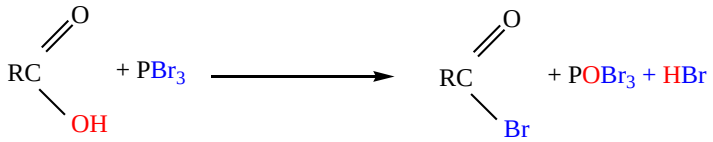
Reactivity of alcohols is in order $1^0 > 2^0 > 3^0$, and the reactivity of carboxylic acids is in order HCOOH› CH_3COOH › RCH_2COOH › $R_2CHCOOH$ › R_3CCOOH, due to steric hindrance. i.e. the presence of bulky groups near the site of reaction, whether in the alcohol or in acid slows esterification.

4. Formation of acid halides

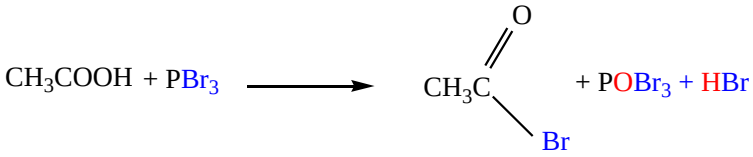
Carboxylic acids (except methanoic acid) react with phosphorus halides to form acid halides



$$RC(=O)OH + PCl_3 \longrightarrow RC(=O)Cl + POCl_3 + HCl$$

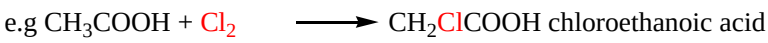


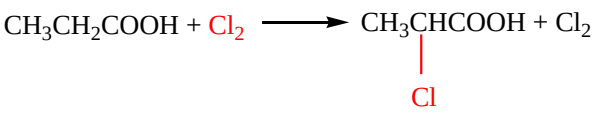
Example



5. Halogenation of aliphatic acids

(a) Carboxylic acids (except methanoic acid) react with chlorine in presence of sunlight or u.v light, thereby a chlorine atom replacing an α-hydrogen.





2-Chloropropanoic acid

(b) Bromine replaces an α-hydrogen in presence of red phosphorous (hell-vohlard zelensky reaction)

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