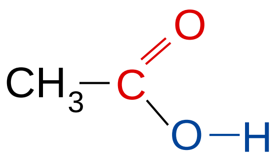
CARBOXYLIC ACIDS

Structure

- contain the carboxyl functional group COOH
- includes a **carb**onyl (**C=O**) group *and* a hydr**oxyl** (**O-H**) group
- the bonds are in a **planar** arrangement
- are isomeric with esters :- RCOOR'



Q.1 *Draw structures for, and name, all* ***carboxylic acids*** *with formula :-*

CH_2O_2 $C_2H_4O_2$ $C_3H_6O_2$ $C_4H_8O_2$ $C_5H_{10}O_2$

Nomenclature **Remove e** from the equivalent alkane and **add . . . OIC ACID .**

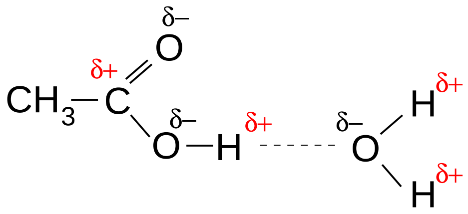
e.g. CH_3COOH is called ethanoic acid as it is derived from ethane.

Many carboxylic acids are still known under their trivial names, some having been called after characteristic properties or origin.

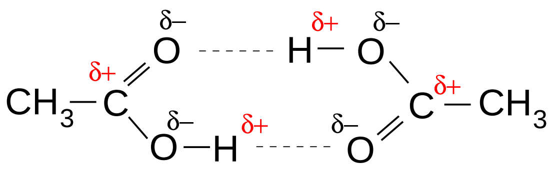
Formula	name	(trivial name)	origin of name
HCOOH	methanoic acid	*formic acid*	latin for ant
CH_3COOH	ethanoic acid	*acetic acid*	latin for vinegar
C_6H_5COOH	benzenecarboxylic acid	*benzoic acid*	from benzene

Physical properties

Solubility
- acids are very soluble in organic solvents
- soluble in water is due to **hydrogen bonding**
- small ones dissolve readily in cold water
- as mass increases, the solubility decreases
- benzoic acid is fairly insoluble in cold but soluble in hot water



Intermolecular hydrogen bonding between ethanoic acid and water



In non-polar solvents, molecules dimerize due to intermolecular hydrogen bonding.

Boiling point
- **increases as size increases -** increased van der Waals forces
- carboxylic acids have high boiling points for their relative mass
- arises from inter-molecular **hydrogen bonding** due to the **polar O—H bonds**
- additional inter-molecular attractions = more energy to separate the molecules

The effect of hydrogen bonding on the boiling point of compounds of similar mass

Compound	Formula	M_r	b. pt. (°C)	Comments
butane	C_4H_{10}	58	-0.5	*basic van der Waals*
propanal	C_2H_5CHO	58	49	+ *dipole-dipole*
propan-1-ol	C_3H_7OH	60	97	+ *hydrogen bonding*
ethanoic acid	CH_3COOH	**60**	**118**	+ *hydrogen bonding*

Preparation
- *Oxidation of aldehydes* — **RCHO + [O] —> RCOOH**
- *Hydrolysis of esters* — **RCOOR + H_2O ⇌ RCOOH + ROH**
- *Hydrolysis of acyl chlorides* — **RCOC*l* + H_2O —> RCOOH + HC*l***
- *Hydrolysis of nitriles* — **RCN + 2 H_2O —> RCOOH + NH_3**
- *Hydrolysis of amides* — **$RCONH_2$ + H_2O —> RCOOH + NH_3**

CHEMICAL PROPERTIES

Acidity • weak monobasic acids $\mathbf{RCOOH + H_2O}(l) \rightleftharpoons \mathbf{RCOO^-}(aq) + \mathbf{H_3O^+}(aq)$

They act as typical acids in the following reactions with...

Metals • Produce a **salt** and **hydrogen**

• $\mathbf{2RCOOH + Mg}(s) \longrightarrow \mathbf{(RCOO^-)_2Mg^{2+}}(aq) + \mathbf{H_2}(g)$

Carbonates • Produce a **salt** and **carbon dioxide**

• $\mathbf{2\ RCOOH + Na_2CO_3}(s) \longrightarrow \mathbf{2\ RCOO^-Na^+}(aq) + \mathbf{CO_2}(g) + \mathbf{H_2O}(l)$

ANALYTICAL USE

Carboxylic acids are strong enough acids to liberate CO_2 from carbonates.
Phenols are also acidic but not are not strong enough to liberate CO_2

Alkalis • form salts with alkalis $\mathbf{RCOOH + NaOH}(aq) \longrightarrow \mathbf{RCOO^-Na^+}(aq) + \mathbf{H_2O}(l)$

The acid can be liberated from its salt by treatment with a stronger acid.

e.g. $\mathbf{RCOO^-Na^+}(aq) + \mathbf{HCl}(aq) \longrightarrow \mathbf{RCOOH + NaCl}(aq)$

Conversion of an acid to its water soluble salt followed by acidification of the salt to restore the acid is often used to separate acids from a mixture.

Esterification Involves the reaction of a carboxylic acid with an alcohol. A **reversible** reaction.

Reagent(s) Alcohol + acid catalyst (eg conc. H_2SO_4)

Conditions Reflux

Equation $\mathbf{CH_3COOH + CH_3OH \rightleftharpoons CH_3COOCH_3 + H_2O}$

ethanoic acid ***methanol*** ***methyl ethanoate***

This is an **example of equilibrium**. Concentrated sulphuric acid not only makes an excellent catalyst but also removes water which will, according to Le Chatelier's Principle, move the equilibrium to the right and produce a bigger yield of ester.

Q.2 *State the compounds needed to synthesise the following three esters;*

propyl ethanoate

ethyl propanoate

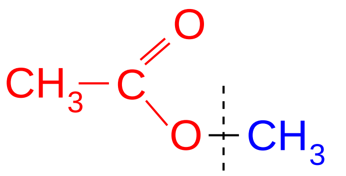
$HCOOC_2H_5$

ESTERS - RCOOR'

Structure Substitute an organic group for the H in acids

Nomenclature first part from alcohol, second part from acid

e.g. ***methyl ethanoate*** CH_3COOCH_3



Q.3 *Draw structures for, and name, all esters of formula $C_4H_8O_2$ and $C_5H_{10}O_2$. From which acid and alcohol are each derived?*

REACTIONS Esters are **unreactive** compared with acids and acyl chlorides.

Hydrolysis $CH_3COOCH_3 + H_2O \rightleftharpoons CH_3COOH + CH_3OH$ reflux in **acid** soln.

$CH_3COOCH_3 + NaOH \longrightarrow CH_3COO^-Na^+ + CH_3OH$ reflux in **alkali**

In the presence of alkali, the carboxylic acid reacts to form a soluble sodium salt

USES Despite being fairly chemically unreactive substances **esters are useful** as ...

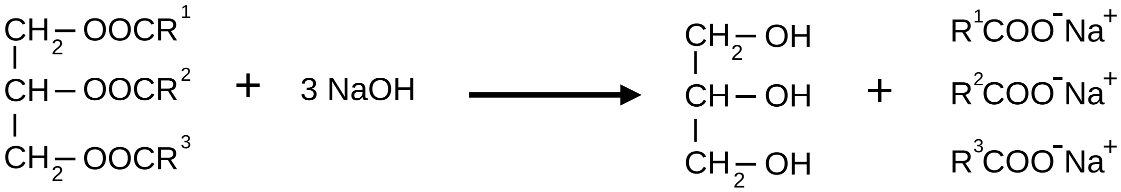
- solvents *eg*
- plasticisers *eg*
- "fruity" food flavouring *eg*

Q.4 *Consult a suitable text book to find some esters with characteristic smells.*

TRIGLYCERIDES AND FATS

Triglycerides
- are the most common component of edible fats and oils
- are triesters of the alcohol glycerol, (propane-1,2,3-triol) and fatty acids

Saponification
- alkaline hydrolysis of triglycerol esters produces soaps
- a simple soap is the salt of a fatty acid
- as most oils contain a mixture of triglycerols, soaps are not pure compounds
- the quality of a soap depends on the oils from which it is made

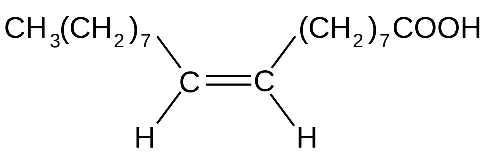


FATTY ACIDS

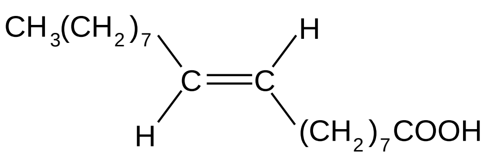
Origin
- carboxylic acids that are obtained from natural oils and fats
- can be **SATURATED** or **UNSATURATED**

Saturated $CH_3(CH_2)_{16}COOH$ octadecanoic acid *(stearic acid)*

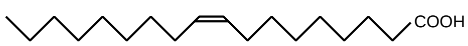
Unsatured 9 $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$ octadec-9-enoic acid *(oleic acid)*

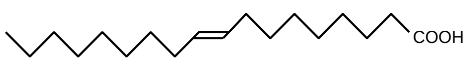


cis isomer

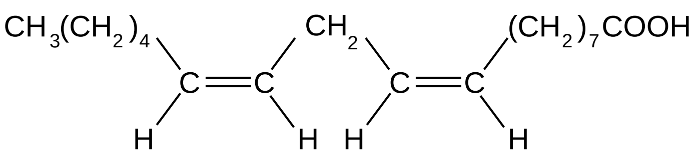


trans isomer





12 9
$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$ octadec-9,12-dienoic acid *(linoleic acid)*



FATTY ACIDS AND HEALTH

Saturated

- solids at room temperature
- found in meat and dairy products
- are bad for health
- known to increase cholesterol levels which can lead to heart problems

Mono unsaturated

- contain just one C=C
- thought to be neutral to our health
- found in olives, olive oil, groundnut oil, nuts and avocados.

Poly unsaturated

- are considered to be 'good fats'
- contain more than one C=C bond
- tend to be liquids at room temperature, eg olive oil.
- can be split into two main types...

1. *Omega 3 - fatty acids* lower the total amount of fat in the blood and can lower blood pressure and decrease the risk of cardiovascular disease.

Ω (omega) end $CH_3CH_2\overset{3}{C}H{=}CHCH_2CH_2CH_2CH_2CH{=}CH(CH_2)_7COOH$

2. *Omega 6 - fatty acids* reduce the risk of cardiovascular disease but can contribute to allergies and inflammation

Ω (omega) end $CH_3CH_2CH_2CH_2CH_2\overset{6}{C}H{=}CHCH_2CH{=}CH(CH_2)_7COOH$

Cholesterol

- a fatty substance which is found in the blood
- it is mainly made in the body
- plays an essential role in how every cell in the body works
- eating too much saturated fat increases cholesterol levels
- too much cholesterol in the blood can increase the risk of heart problems

Reducing levels

- cut down on saturated fats and trans fats
  (trans fats are more stable and are difficult to break down in the body)
- replace them with monounsaturated fats and polyunsaturated fats
- eat oily fish
- have a high fibre diet; *porridge, beans, fruit and vegetables*
- exercise regularly

BIOFUELS

What are they? Liquid fuels made from plant material and recycled elements of the food chain

- **biodiesel** diesel alternative
- **bioethanol** petrol additive / substitute

Biodiesel

What is it? Biodiesel is an alternative fuel which can be made from waste vegetable oil or from oil produced from seeds. It can be used in any diesel engine, either neat or mixed with petroleum diesel.

It is a green fuel, does not contribute to the carbon dioxide (CO_2) burden and produces drastically reduced engine emissions. It is non-toxic and biodegradable.

Advantages

- renewable - derived from sugar beet, rape seed
- dramatically reduces emissions
- carbon neutral
- biodegradable
- non-toxic
- fuel & exhaust emissions are less unpleasant
- can be used directly in unmodified diesel engine
- high flashpoint - safer to store & transport
- simple to make
- used neat or blended in any ratio with petroleum diesel

Disadvantages

- poor availability - very few outlets & manufacturers
- more expensive to produce
- poorly made biodiesel can cause engine problems

Future problems

- there isn’t enough food waste to produce large amounts of biodiesel
- crops grown for biodiesel use land for food crops
- a suitable climate is needed to grow most crops
- some countries have limited water resources

Q.4 *Is it sensible, in a world that is short of food, that land should be turned over to the production of biofuels? What are your ideas?*