FACTFILE:
GCE CHEMISTRY

4.8 CARBOXYLIC ACIDS

Rewarding Learning

Learning Outcomes

Students should be able to:

4.8.1 recall the structural formulae of carboxylic acids, including branched structures, with up to six carbon atoms in the main chain;

4.8.2 explain the boiling points and solubility of carboxylic acids by making reference to intermolecular attractions;

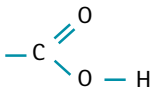
4.8.3 recall that carboxylic acids can be prepared from primary alcohols and aldehydes to include practical details;

4.8.4 recall that carboxylic acids, or their salts, can also be formed by acid or base catalysed hydrolysis of esters and nitriles; and

4.8.5 recall that carboxylic acids form salts with sodium carbonate, sodium hydroxide and ammonia.

Nomenclature of carboxylic acids

The functional group is called the **carboxyl** group and is drawn

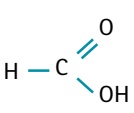


or is written –COOH. It is made of a carbonyl and hydroxyl group.

The names are based on the carbon skeleton with the ending changed from –**ane** to – **anoic acid**. IUPAC nomenclature rules state that *the carboxyl carbon in the COOH functional group is always carbon number 1*. Any substituents are numbered based on this.

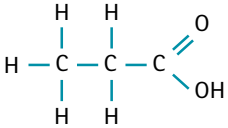
Some carboxylic acids are shown below:

HCOOH



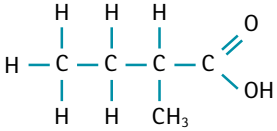
methanoic acid

CH_3CH_2COOH



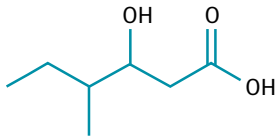
propanoic acid

$CH_3CH_2CH(CH_3)COOH$



2-methylbutanoic acid

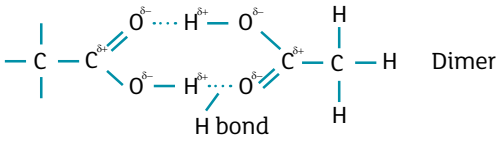
The structure below is the skeletal formula for 3-hydroxy-4-methylhexanoic acid.



Physical properties

1. The boiling point is higher than that of the corresponding alkane. This is because the intermolecular forces between alkanes are van der Waals' forces but between carboxylic acid molecules there are van der Waals' and hydrogen bonds which are stronger.

   The boiling point is higher than that of the corresponding alcohol. This is because each pair of carboxylic acid molecules is held together by 2 hydrogen bonds in a structure called a dimer. This doubles the size of the molecule and increases the van der Waals forces between the dimers resulting in a higher boiling point.



Dimer

2. Short chain carboxylic acids are soluble (miscible) in water as the polar OH and O can hydrogen bond with water. As the number of carbon atoms in the chain increases the solubility decreases because the longer hydrocarbon "tails" of the molecules get between water molecules and break hydrogen bonds

Acid reactions of carboxylic acids

Carboxylic acids take part in typical acid reactions – with carbonates, metals and bases to form salts. The salts are - anoates

1. With carbonates and hydrogencarbonates

acid + carbonate → salt + carbon dioxide + water
e.g.

$$2CH_3COOH + Na_2CO_3 \rightarrow 2CH_3COONa + CO_2 + H_2O$$

ethanoic acid; sodium carbonate; sodium ethanoate; carbon dioxide; water

acid + hydrogencarbonate → salt + carbon dioxide + water

$$CH_3COOH + NaHCO_3 \rightarrow CH_3COONa + CO_2 + H_2O$$

ethanoic acid; sodium hydrogencarbonate; sodium ethanoate; carbon dioxide; water

e.g.
This reaction can be used to test for the presence of an acid.

When solid sodium carbonate reacts with a carboxylic acid, effervescence is observed as carbon dioxide is produced.

2. with bases

acid + base → salt + water
e.g.

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

ethanoic acid; sodium hydroxide; sodium ethanoate; water

observations: The mixture warms up.

3. with ammonia

$$CH_3COOH + NH_3 \rightarrow CH_3COONH_4$$

ethanoic acid; ammonia; ammonium ethanoate

observations: the smell of ammonia disappears.

When dibasic or tribasic acids react with excess reagent, then all of the COOH groups react.

Reaction with phosphorus pentachloride PCl_5

PCl_5 replaces an OH group with a Cl. A new organic substance called an acyl chloride RCOCl, is formed. In addition $POCl_3$, phosphorus(V) trichloride oxide and hydrogen chloride are produced.

For example:

$$\underset{\text{propanoic acid}}{CH_3CH_2COOH} + PCl_5 \rightarrow \underset{\text{propanoyl chloride}}{CH_3CH_2COCl} + POCl_3 + HCl$$

Condition: room temperature
Observation: mixture warms up, steamy/misty fumes of hydrogen chloride, solid disappears.

Reduction reactions
Carboxylic acids are reduced to aldehdyes and further reduced to primary alcohols. The reducing agent is lithium tetrahydridoaluminate(III) (lithal).

$$\underset{\text{propanoic acid}}{CH_3CH_2COOH} + 2[H] \rightarrow \underset{\text{propanal}}{CH_3CH_2CHO} + H_2O$$

$$\underset{\text{propanoic acid}}{CH_3CH_2COOH} + 4[H] \rightarrow \underset{\text{propan-1-ol}}{CH_3CH_2CH_2OH} + H_2O$$

Condition: If the aldehyde is required it is distilled off, but prolonged refluxing with $LiAlH_4$ in ether will produce the primary alcohol.

Preparation of carboxylic acids

1. From primary alcohols or aldehydes

For example:

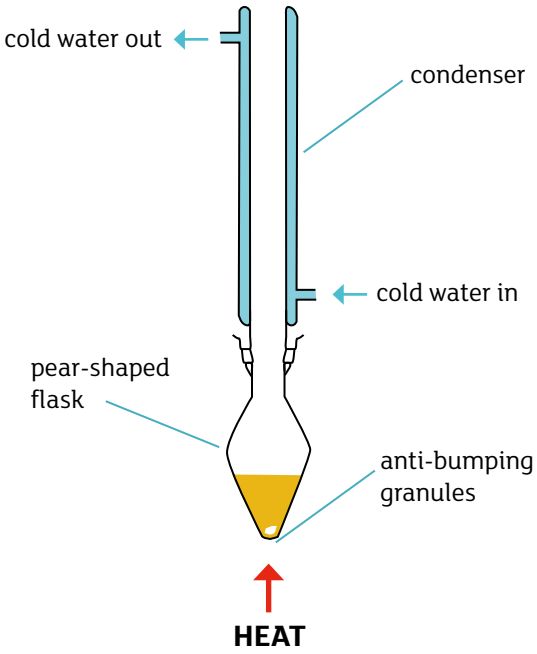
$$\underset{\text{ethanol}}{CH_3CH_2OH} + 2[O] \rightarrow \underset{\text{ethanoic acid}}{CH_3COOH} + H_2O$$

Alternatively an aldehyde may be used to produce the corresponding acid.

For example:

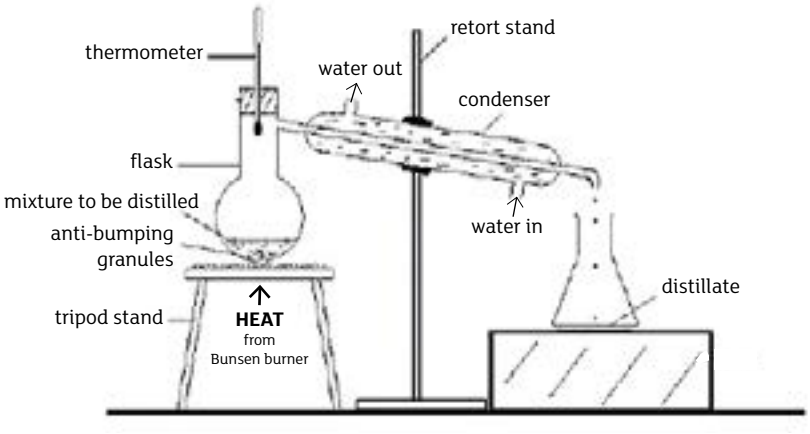
$$\underset{\text{ethanal}}{CH_3CHO} + [O] \rightarrow \underset{\text{ethanoic acid}}{CH_3COOH}$$

- Add concentrated sulfuric acid to water in a pear shaped/round bottomed flask.
- Swirl the solution and cool the flask to dissipate the heat and prevent spitting.
- Add potassium dichromate(VI) and swirl.
- Add anti-bump granules to promote smooth boiling.
- Add the alcohol slowly, to the acidified potassium dichromate(VI) solution and cool in a water bath.
- Heat the mixture under reflux. (reflux is the repeated boiling and condensing of a reaction mixture).
- Distil off the acid.



A labelled diagram of reflux should include

- Condenser in upright position
- Flask
- Heat source
- Water flowing correctly in condenser
- Anti-bumping granules
- Any gaps at the joints or closed apparatus will be penalised



A labelled diagram of distillation should include

- Condenser in horizontal position
- Flask
- Side arm connection
- Thermometer
- Heat source
- Water flowing correctly through the condenser
- Anti-bumping granules
- Any gaps at the joints or a closed apparatus are penalised

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2. From acid or base catalysed hydrolysis of esters

Hydrolysis is the breaking up of molecules by reaction with water. It is slow so often it is catalysed by adding acid or base. An ester can be hydrolysed into an alcohol and a carboxylic acid.

using acid

$$\underset{\text{ethyl ethanoate}}{CH_3COOCH_2CH_3} + H_2O \overset{H^+(aq)}{\rightleftharpoons} \underset{\text{ethanoic acid}}{CH_3COOH} + \underset{\text{ethanol}}{CH_3CH_2OH}$$

Condition: reflux with dilute hydrochloric acid

In the base catalysed reaction the salt of the acid is formed, acid is then added to it to liberate the free carboxylic acid. There are two advantages of base hydrolysis:

- the reactions are one-way rather than reversible, and
- the products are easier to separate.

$$\underset{\text{ethyl ethanoate}}{CH_3COOCH_2CH_3} + NaOH \rightarrow \underset{\text{sodium ethanoate}}{CH_3COONa} + \underset{\text{ethanol}}{CH_3CH_2OH}$$

3. From acid or base catalysed hydrolysis of nitriles

Nitriles are compounds which contain the –C≡N functional group.

For example:
ethanenitrile CH_3CN propanenitrile CH_3CH_2CN

Nitriles react with water in two stages

- first to produce an **amide** (-$CONH_2$ functional group),
- and then **the ammonium salt of a carboxylic acid**.

For example, ethanenitrile would produce ammonium ethanoate via ethanamide.

$$CH_3CN \xrightarrow{H_2O} CH_3CONH_2 \xrightarrow{H_2O} CH_3COONH_4$$

Acid hydrolysis of nitrile

$$CH_3CN + 2H_2O + HCl \longrightarrow CH_3COOH + NH_4Cl$$

Condition: reflux with dilute hydrochloric acid.

To produce the carboxylic acid in this case, add dilute hydrochloric acid or dilute sulfuric acid.

Base hydrolysis of nitrile

$$CH_3CN + NaOH + H_2O \rightarrow CH_3COONa + NH_3$$

Condition: reflux with sodium hydroxide solution.

Revision Questions

1 Which one of the following compounds reacts with propanoic acid to form propanoyl chloride?

A chlorine

B chloropropane

C hydrogen chloride

D phosphorus pentachloride [1]

2 Lauric acid, $C_{11}H_{23}COOH$, the main acid found in coconut oil, is also found in macadamia nuts. It is a white solid at room temperature with a melting point of 45°C, and is insoluble in water.

a) Write the empirical formula for lauric acid.

..... [1]

b) Explain why ethanoic acid is soluble in water where as lauric acid is insoluble.

.....

.....

..... [3]

c) Describe a chemical test to prove that lauric acid is an acid.

.....

.....

..... [2]

d) Write an equation for the reaction of lauric acid with phosphorus pentachloride

..... [2]

e) Lauric acid can be reduced to the corresponding alcohol.

(i) Write an equation for the reduction using [H] to represent the reducing agent.

..... [2]

(ii) Name a suitable reducing agent.

..... [1]

3 a) **Write equations** for the reaction of

propanoic acid and magnesium

..... [1]

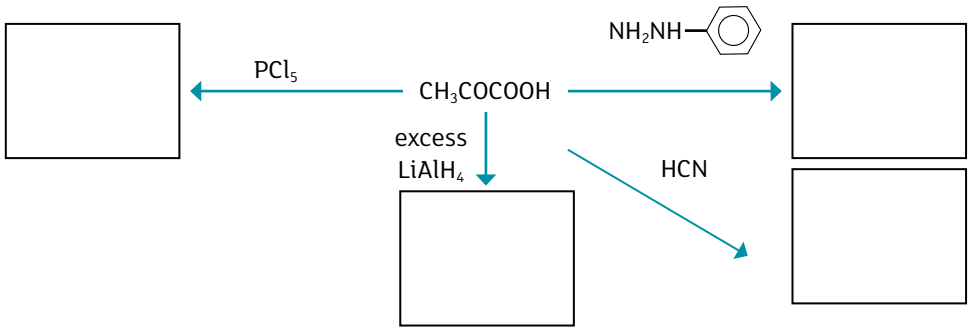
methanoic acid and sodium carbonate

..... [1]

butanoic acid and potassium hydroxide

..... [1]

b) Pyruvic acid shows both the reactions of a ketone and a carboxylic acid. Complete the following flow sequences below showing the oranic product in each case.



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