VICTORIA JUNIOR COLLEGE
CHEMISTRY DEPARTMENT

JC2 H2 CHEMISTRY
CARBOXYLIC ACIDS & DERIVATIVES

Lecture Outline

Part I: Carboxylic Acids

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https://for.edu.sg/chem2025carboxyl

scan this QR code to ask questions related to the lecture

Part II: Acid Derivatives (Esters and Acyl Chlorides)

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4 Summary of Reactions of Acid Derivatives

Assessment Objectives

Students should be able to:

(a) Describe the formation of carboxylic acids from alcohols, aldehydes and nitriles

(b) Describe the reactions of carboxylic acids in the formation of:

- **(i)** salts
- **(ii)** esters on condensation with alcohols, using ethyl ethanoate as an example
- **(iii)** acyl chlorides, using ethanoyl chloride as an example
- **(iv)** primary alcohols, via reduction with lithium aluminium hydride, using ethanol as an example

(c) Explain the acidity of carboxylic acids and of chlorine–substituted ethanoic acids in terms of their structures

(d) Describe the hydrolysis of acyl chlorides

(e) Describe the condensation reactions of acyl chlorides with alcohols, phenols and primary amines

(f) Explain the relative ease of hydrolysis of acyl chlorides, alkyl chlorides and aryl chlorides

(g) Describe the formation of esters from the condensation reaction of acyl chlorides, using phenyl benzoate as an example

(h) Describe the acid and base hydrolysis of esters

References

(a) Introduction to Organic Chemistry by GI Brown

(b) Principles of Organic Chemistry by Peter RS Murray

(c) Organic Chemistry by Morrison and Boyd

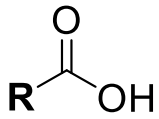
(d) Organic Chemistry by TW Graham Solomons

Part I: Carboxylic Acids

1 Introduction

Structure

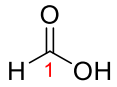
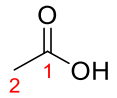
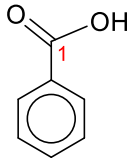
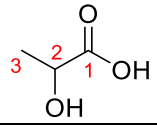
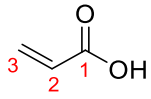
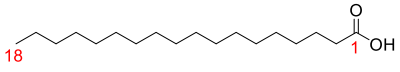
- General formula of monocarboxylic acids is $C_nH_{2n}O_2$
- Functional group is a **carboxyl** functional group, –COOH or $–CO_2H$, which contains both a carbonyl group and a hydroxyl group; hence the name.
- Carboxylic acids are represented as **R**CO_2H, where **R** = H, alkyl or aryl group.



Nomenclature

1. find the longest alkyl chain, which is the parent chain, that contains the carboxyl group
2. the *'e'* of the *–ane* of the alkane with the same number of carbon atoms as the parent chain is replaced by *'oic acid'*. Note that it is not required to number the position of the carboxyl group as it is assigned position 1 within the chain.
3. identify substituent(s), if any, on the parent chain and include its position as prefixes to the name of the parent chain

Examples

IUPAC name (common name)	structural formula	skeletal formula
methanoic acid (formic acid)	HCO_2H	
ethanoic acid (acetic acid)	CH_3CO_2H	
benzoic acid (benzenecarboxylic acid)	$C_6H_5CO_2H$	
2-hydroxypropanoic acid (lactic acid)	$CH_3CH(OH)CO_2H$	
prop–2–enoic acid (acrylic acid)	$CH_2=CHCO_2H$	
octadecanoic acid (stearic acid)	$CH_3(CH_2)_{16}CO_2H$	

2 Physical Properties

2.1 Boiling Point

- The lower members are liquids with pungent odours.
- Example: ethanoic acid (vinegar), butanoic acid (rancid butter, human sweat)

> 🔍 **Fun Fact:** Body odour begins with secretions from the apocrine glands, located mostly in the armpits. Skin bacteria use these secretions to produce energy and waste products, among which is 3–methyl–2–hexenoic acid, $CH_3CH_2CH_2C(CH_3)=CHCO_2H$, which is largely responsible for body odour. Each individual's sweat glands also produce a characteristic blend of carboxylic acids which can be detected by the sensitive nose of a dog.

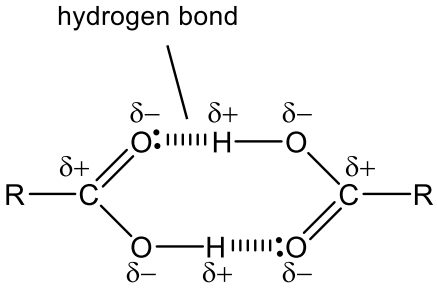
- Boiling point **increases** with increasing molecular size and number of electrons per molecule (Recall: Molecular size increases with M_r).

compound	M_r	boiling point / °C
CH_3CO_2H	60	118
$CH_3(CH_2)_2CO_2H$	88	164

- Carboxylic acids are **less volatile** (higher boiling point) than alcohols of similar M_r.

compound	M_r	boiling point / °C
CH_3CO_2H	60	118
$CH_3CH(OH)CH_3$	60	97

  - Carboxylic acids form **stronger hydrogen bonding** than alcohols because the O–H bond is more polarised due to the presence of electron–withdrawing inductive C=O group.
  - Furthermore, carboxylic acid molecules **dimerise** in the liquid state and in non–polar solvents, forming two hydrogen bonds between each pair of molecules.



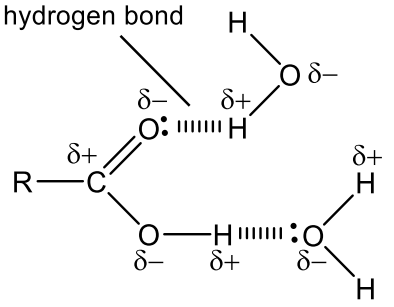
dimer

  - However, in polar solvents such as water, the molecules exist as monomers and dissociate to some extent into H^+ and $\mathbf{R}CO_2^-$.

$$\mathbf{R}CO_2H \rightleftharpoons \mathbf{R}CO_2^- + H^+$$

2.2 Solubility

- Lower acids are completely **miscible** with water because of the ability of the $–CO_2H$ group to form **hydrogen bonds** with water.



- As the length of the non-polar **hydrocarbon chain** increases, solubility in water decreases. Example: benzoic acid is only slightly soluble in cold water but dissolves readily in hot water.
- In contrast, the solubility of the carboxylic acids in non-polar solvents increases as the non-polar hydrocarbon chain length increase.

2.3 Acidity

Students should be able to
c) explain the acidity of carboxylic acids and of chlorine–substituted ethanoic acids in terms of their structures

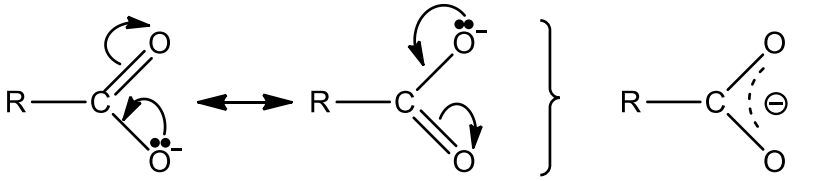
- Carboxylic acids are generally considered *weak acids*.
- Being a weak acid, carboxylic acids partially dissociate by the following equation:

$$\mathbf{R}CO_2H \rightleftharpoons H^+ + \mathbf{R}CO_2^-$$

- The carboxylate anion can be resonance stabilised due to the delocalisation of electrons around the *–COO⁻* group.

$$\mathbf{R}CO_2H \rightleftharpoons H^+ + \mathbf{R}CO_2^-$$

resonance stabilisation is minimal — *highly stabilised by resonance*



resonance structures — resonance hybrid

Note:

- C–O bonds are equal in length. The negative charge is equally distributed between the two oxygen atoms, leading to a stabilisation of the carboxylate anion.

Strength of carboxylic acids

Consider the dissociation of a weak acid H**A**: $HA \rightleftharpoons H^+ + A^-$

When A^- is more stable, there is a **greater** tendency for H**A** to dissociate. H**A** would then be a **stronger** acid. Thus, the strength of the carboxylic acid RCO_2H depends on the **stability of RCO_2^-** ion.

An **electron–withdrawing inductive group** in RCO_2^- reduces the electron density of the negative charge on the carboxylate anion by **charge dispersal**. This **stabilises** the RCO_2^- and **increases** the **strength** of the acid.

An **electron–donating inductive group** does the reverse.

- *pK_a of some carboxylic acids*

formula	pK_a	formula	pK_a
HCO_2H	3.75	$ClCH_2CO_2H$	2.86
CH_3CO_2H	4.76	Cl_2CHCO_2H	1.29
$CH_3CH_2CO_2H$	4.82	Cl_3CCO_2H	0.65
$CH_3CH_2CH_2CO_2H$	4.87	FCH_2CO_2H	2.60
$C_6H_5CO_2H$	4.20	$N{\equiv}CCH_2CO_2H$	2.50

Recall:

- smaller $pK_a \Rightarrow$ larger $K_a \Rightarrow$ greater extent of acid dissociation $\Rightarrow$ stronger acid

Worked Example 1

Why are carboxylic acids stronger acids than alcohols in general?

Answer:

$RCO_2H \rightleftharpoons H^+ + RCO_2^-$ --- (1)

$ROH \rightleftharpoons H^+ + RO^-$ ---- (2)

In **R**CO_2^- ion, the ..... in the $-CO_2^-$ group ..... with one another, allowing delocalisation and resulting in **R**CO_2^- ion having a ..... structure. This helps to disperse the negative charge on the O atom, hence ..... the **R**CO_2^- ion and ..... the strength of the acid **R**CO_2H.

The **R**O^- ion is ..... by ..... inductive effect of the **R** group, which causes the negative charge to be .....

The first equilibrium position lies greater to the ..... compared to the second. Hence, **R**CO_2H is a ..... acid than ROH.

Worked Example 2

Arrange the following carboxylic acids in order of increasing acid strength.

I	butanoic acid	$CH_3CH_2CH_2CO_2H$
II	2–chlorobutanoic acid	$CH_3CH_2CHClCO_2H$
III	2–bromobutanoic acid	$CH_3CH_2CHBrCO_2H$
IV	3–bromobutanoic acid	$CH_3CHBrCH_2CO_2H$

Answer:

The more stable the $\mathbf{RCO_2^-}$, the greater the extent of acid dissociation and the stronger the acid.

Since the electronegative C*l* and Br exert **electron-withdrawing inductive effect**, the corresponding RCO_2^- is stabilised by charge dispersal. Since C*l* is **more electronegative**, $CH_3CH_2CHClCO_2^-$ is more stable than $CH_3CH_2CHBrCO_2^-$.

Between $CH_3CH_2CH\mathbf{Br}CO_2^-$ and $CH_3CH\mathbf{Br}CH_2CO_2^-$, $CH_3CH_2CH\mathbf{Br}CO_2^-$ is more stabilised since the electron-withdrawing group is **closer** to the negative charge on the carboxylate ion.

Hence, the carboxylic acids in increasing acid strength:

3 Laboratory Preparation

Students should be able to

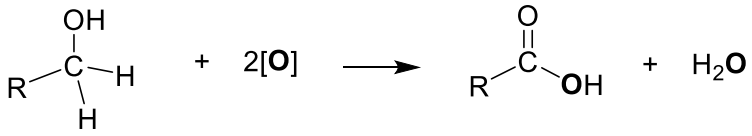
a) Describe the formation of carboxylic acids from alcohols, aldehydes and nitriles

3.1 Oxidation of Primary Alcohols and Aldehydes

Oxidation of primary (1°) alcohol to **carboxylic acid**

Type of reaction: **Oxidation**

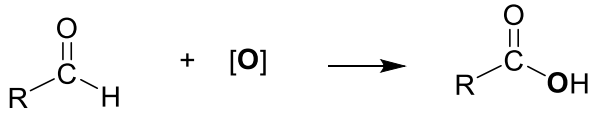
Reagents and conditions: **$K_2Cr_2O_7$(aq), H_2SO_4(aq), heat under reflux**
or **$KMnO_4$(aq), H_2SO_4(aq), heat**



Oxidation of aldehyde to **carboxylic acid**

Type of reaction: **Oxidation**

Reagents and conditions: **$K_2Cr_2O_7$(aq), H_2SO_4(aq), heat**
or **$KMnO_4$(aq), H_2SO_4(aq), heat**

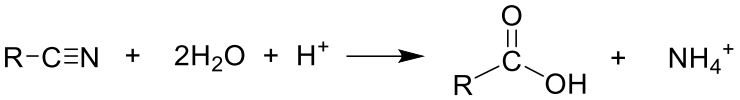


3.2 Hydrolysis of Nitriles

<u>Acid hydrolysis of nitrile</u> to **<u>carboxylic acid</u>**

Type of reaction: **Hydrolysis**

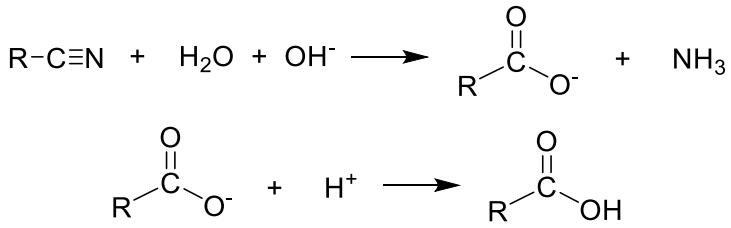
Reagents and conditions: **H_2SO_4(aq), heat**



<u>Alkaline hydrolysis of nitrile</u> to **<u>carboxylic acid via carboxylate salt</u>**

Type of reaction: **Hydrolysis**

Reagents and conditions: **NaOH(aq), heat, followed by H_2SO_4(aq)**



- Reaction can be seen as taking place via the amide:

RC≡N + H_2O → **R**$CONH_2$
R$CONH_2$ + H_2O → **R**$CO_2^-NH_4^+$

R$CO_2^-NH_4^+$ + H^+ → **R**CO_2H + NH_4^+
R$CO_2^-NH_4^+$ + OH^- → **R**CO_2^- + NH_3 + H_2O

Note:

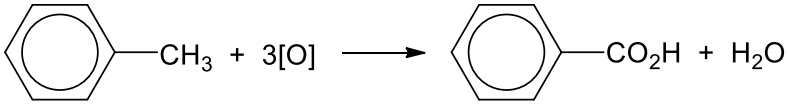
- **Alkaline hydrolysis** of nitrile can be used as a **distinguishing test** as **NH_3** is produced which turns damp red litmus blue.

3.3 Benzoic Acid Formation from Alkylbenzene

<u>Side-chain oxidation of alkylbenzene to benzoic acid</u>

Type of reaction: **Oxidation**

Reagents and conditions: **$KMnO_4$(aq), H_2SO_4(aq), heat**
or **$KMnO_4$(aq), NaOH(aq), heat, followed by H_2SO_4(aq)**



Note:

- Not confined to methylbenzene as longer side-chains with benzylic hydrogen can also be oxidised and converted to $–CO_2H$.
- In acidic medium, **decolourisation** of purple solution ($KMnO_4$) and **white precipitate** (benzoic acid) is formed.

Worked Example 3 (J90/I/28)

The same carboxylic acid is obtained either by the hydrolysis of a nitrile **P** or by the oxidation of an alcohol **Q**. Which of the following pairs could be **P** and **Q**?

	P	**Q**
A	CH_3CH_2CN	CH_3CH_2OH
B	$(CH_3)_2CHCN$	$(CH_3)_3COH$
C	$C_6H_5CH(CH_3)CN$	$C_6H_5CH_2CH_2OH$
D	$C_6H_5CH_2CN$	$C_6H_5CH_2CH_2OH$

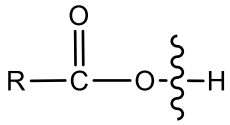
Answer:

4 Reactions

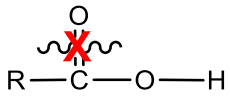
Students should be able to

b) Describe the reactions of carboxylic acids in the formation of: (i) salts, (ii) esters on condensation with alcohols, using ethyl ethanoate as an example, (iii) acyl chlorides, using ethanoyl chloride as an example, (iv) primary alcohols, via reduction with lithium aluminium hydride, using ethanol as an example

- The characteristic chemical behaviour of carboxylic acids is determined by the functional group, $–CO_2H$.
- The C=O and –OH groups of the carboxyl group are in such close proximity that they modify each other's properties. Hence, carboxylic acids **do not** behave exactly like carbonyl compounds or alcohols.
- The reactions of carboxylic acids almost invariably involve the –OH group, which either undergoes the **loss of a proton** (acts as an acid) or is **substituted** by another atom or group; but does so in a way that is possible only because of the effect of the C=O group.

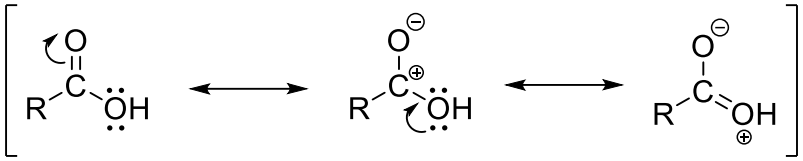


- The C=O group in carboxylic acids **does not** undergo **addition** reactions, e.g. with HCN, which are characteristic of aldehydes and ketones.



Reason:

- **Lone pair of electrons** in p orbital in O of hydroxyl group interacts with the p orbital of the carbonyl C atom. This results in an increase in **delocalisation of electrons** and greater stability. This stability would be lost if a reagent is added the carbonyl group. Thus, carboxylic acids are more resistant to addition than aldehydes and ketones.

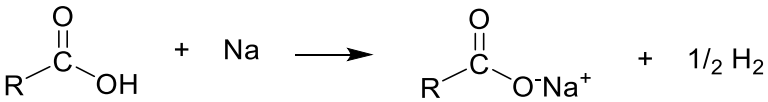


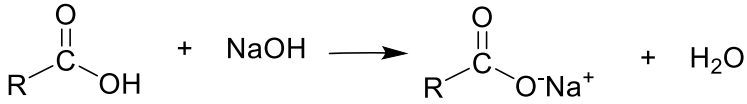
4.1 Salt Formation (as an acid)

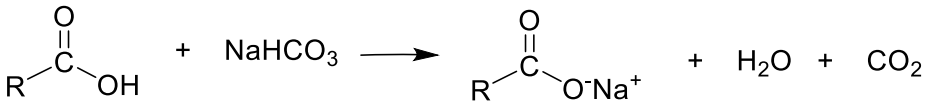
<u>Formation of carboxylate salt from carboxylic acid</u>

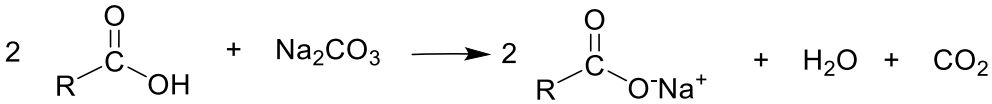
Type of reaction: **redox** (for Na) *or* **neutralisation** (for NaOH, $NaHCO_3$ & Na_2CO_3)

Reagents and conditions: **Na or NaOH or $NaHCO_3$ or Na_2CO_3**









- Carboxylic acids react with carbonates and hydrogen carbonates to liberate CO_2. This **distinguishes** them **from phenols and alcohols**, which are unable to do so.
- Reaction with **Na_2CO_3 or $NaHCO_3$** is a **test for RCO_2H**.
  Effervescence of CO_2 is observed, which gives a **white precipitate** with limewater.

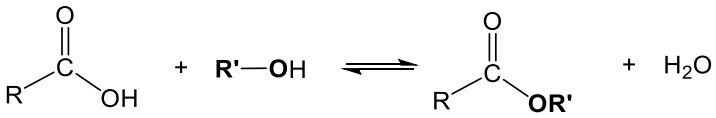
4.2 Condensation to form Ester

<u>Condensation of carboxylic acid with alcohol to form ester</u>

Type of Reaction: **Condensation**

Reagents and conditions: **R'OH with concentrated H_2SO_4 as catalyst, heat**

*(**RECALL!**: A condensation reaction is a reaction in which two molecules combine to form a single molecule with loss of a small molecule such as H_2O, HCl etc.)*



e.g. $CH_3CO_2H + CH_3OH \rightleftharpoons CH_3CO_2CH_3 + H_2O$
methyl ethanoate

e.g. $CH_3CO_2H + CH_3CH_2CH_2OH \rightleftharpoons CH_3CO_2CH_2CH_2CH_3 + H_2O$
propan-1-ol *prop-1-yl ethanoate*

Note:

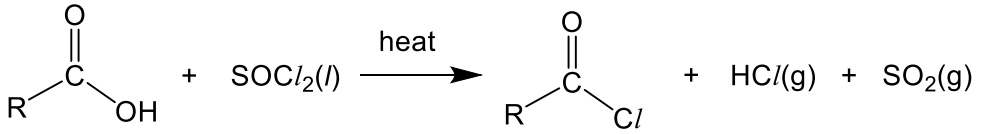
- The reaction is **reversible** as water can act as a nucleophile to attack the electron-deficient carbonyl carbon in the ester and reform the carboxylic acid.
- Notice that the **O** in the **R'O**H remained with the alkoxy part of the ester, while the O in the H_2O originated from the RCO_2H.
- Concentrated H_2SO_4 is used as a **catalyst** to speed up the reaction. It also acts as a dehydrating agent by removing H_2O from the equilibrium and thereby shifting the position of equilibrium to the right to result in a greater yield of the ester.

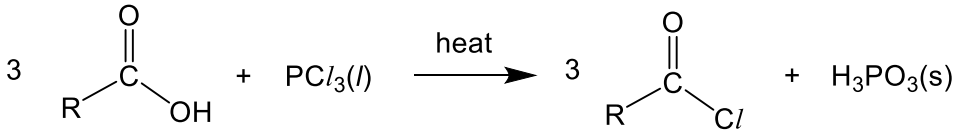
4.3 Conversion to Acyl Chlorides

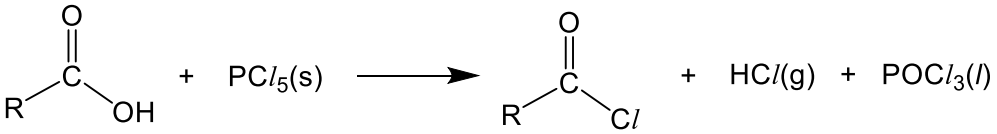
Conversion of carboxylic acid to acyl chloride

Type of Reaction: **Nucleophilic (acyl) substitution**

Reagents and conditions: **SO*Cl*$_2$, heat**
or **PC*l*$_3$, heat**
or **PC*l*$_5$**







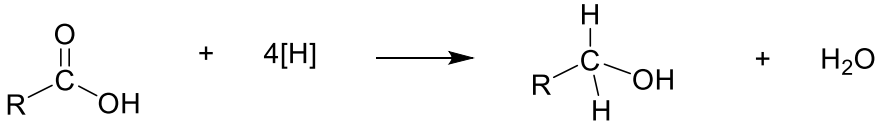
- **Note**: White fumes of HC*l* is observed for SOCl_2 and PCl_5. The reaction with SOCl_2 is especially convenient ('cleaner') as the other two products are both gaseous and are easily removed from the reaction mixture.

4.4 Reduction to Primary Alcohols

Reduction of carboxylic acid to primary (1°) alcohol

Type of Reaction: **Reduction**

Reagents and conditions: **LiA*l*H$_4$ in dry ether**



e.g. $CH_3CO_2H + 4[H] \rightarrow CH_3CH_2OH + H_2O$

- **Note**: Primary alcohols and aldehydes can be oxidised to carboxylic acids, but carboxylic acids can only be reduced back to primary alcohols and not aldehydes.

- Reduction is **more difficult** compared to aldehydes and ketones. Hence, catalytic hydrogenation (i.e. H_2 with Ni or Pt/Pd catalyst) and $NaBH_4$ in ethanol **does not** reduce RCO_2H but it can reduce aldehydes and ketones.

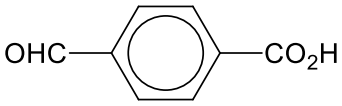
  E.g. using $NaBH_4$ in ethanol,
  $C_6H_5CH_2\mathbf{CO}CH_2\mathbf{CO_2H} + 2[\mathbf{H}] \rightarrow C_6H_5CH_2C\mathbf{H}(O\mathbf{H})CH_2\mathbf{CO_2H}$

- Considering $LiAlH_4$ and $NaBH_4$ as the sources of the hydride anion, H^-, $LiAlH_4$ is the stronger reducing agent of the two. This is due to the larger electronegativity difference between the H and the Al (as compared to between H and B), making the H more electron rich.

Worked Example 4

Identify the organic product of the reaction between $LiAlH_4$ in dry ether and each of the following organic compounds.

(i) $CH_3CH_2CH_2CO_2H$ →

(ii)  →

4.5 Decarboxylation to Alkanes

Decarboxylation of carboxylic acid to alkane

Type of Reaction: **Decarboxylation**

Reagents and conditions: **soda lime, heat**
(soda lime (CaO/NaOH mixture) behaves chemically like NaOH)

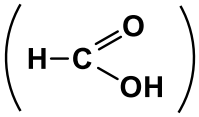
Step 1: $\mathbf{R}CO_2H + NaOH \rightarrow \mathbf{R}CO_2^-Na^+ + H_2O$

Step 2: $\mathbf{R}CO_2^-Na^+ + NaOH \rightarrow \mathbf{R}H + Na_2CO_3$

Overall: $\mathbf{R}CO_2H + 2NaOH \rightarrow \mathbf{R}H + Na_2CO_3 + H_2O$

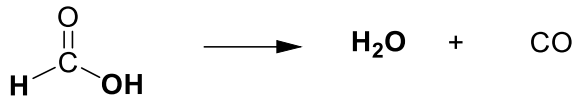
You are now ready to attempt Tutorial Questions 1 to 4.

5 Special Reactions (Dehydration and Oxidation)

5.1 Methanoic Acid 

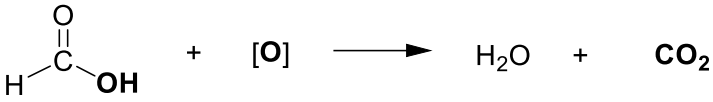
Type of Reaction: **Dehydration**

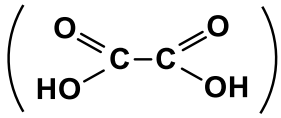
Reagents and conditions: **Excess concentrated H_2SO_4, heat**



Type of Reaction: **Oxidation**

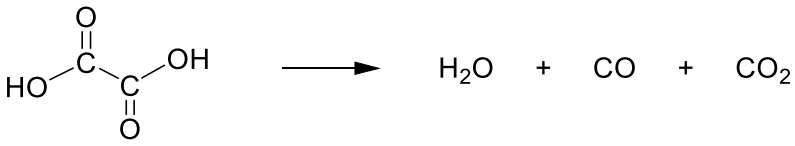
Reagents and conditions: **$KMnO_4$(aq), H_2SO_4(aq), heat**



5.2 Ethanedioic Acid 

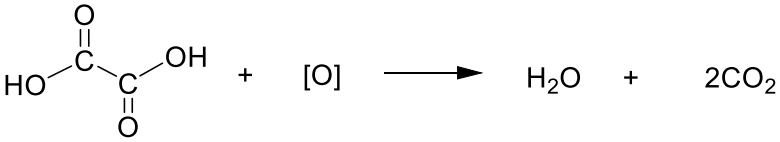
Type of Reaction: **Dehydration**

Reagents and conditions: **Excess concentrated H_2SO_4, heat**

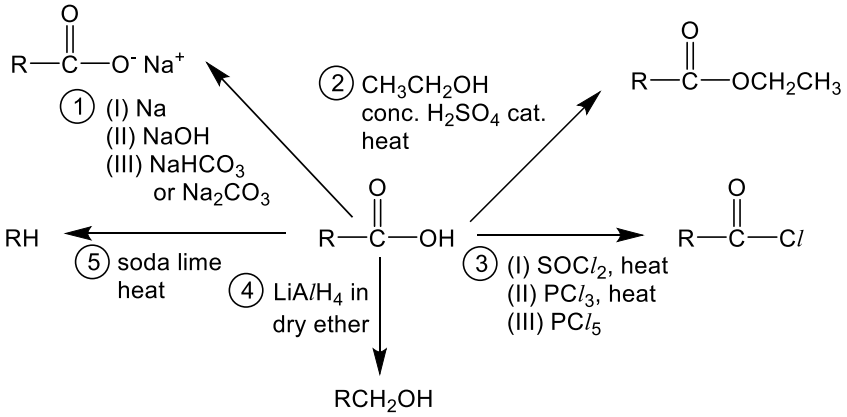


Type of Reaction: **Oxidation**

Reagents and conditions: **$KMnO_4$(aq), H_2SO_4(aq), heat**



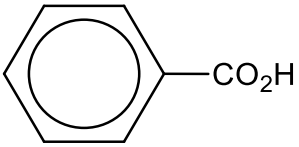
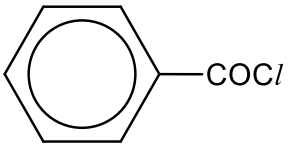
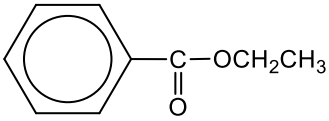
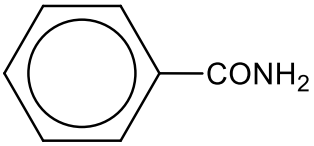
6 Summary of Reactions of Carboxylic Acids



Part II: Acid Derivatives (Esters and Acyl Chlorides)

1 Introduction

- The names are taken in simple ways from the name of the corresponding carboxylic acid.

			Change in name
Carboxylic Acid	CH_3CO_2H ethan*oic acid*	 benz*oic acid*	–
Acyl Chloride	CH_3COCl ethanoyl chloride	 benzoyl chloride	'*–oic acid'* to **'*–oyl chloride'***
Ester	$CH_3CO_2CH_2CH_3$ ethyl ethanoate	 ethyl benzoate	'*–oic acid'* to **'*–oate'*** preceded by name of alcohol as *alkyl*
Amide	CH_3CONH_2 ethanamide	 benzamide	'*–oic acid'* to **'*–amide'***

2 Physical Properties

2.1 Boiling Point

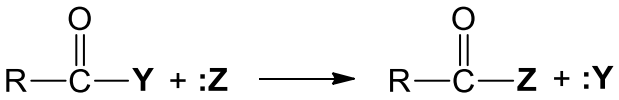
- Acyl chlorides and esters **do not form intermolecular hydrogen bonds** as they lack a hydrogen atom attached directly to a highly electronegative oxygen atom. These **polar** molecules attract each other by weaker **permanent dipole-permanent dipole interactions**. Hence, they have lower boiling points, i.e. are more volatile, than the parent carboxylic acids.
- Amides have a $–NH_2$ group and possess a high degree of **intermolecular hydrogen bonding**. They have higher boiling points, i.e. are less volatile, than the other acid derivatives and exist as solids at room temperature.

2.2 Solubility

- As a result of hydrogen bonding, lower amides are fairly soluble in water and virtually insoluble in hydrocarbon solvents.
- For esters, their solubility varies with the R groups. Generally, they have lower solubility in water than amides since they can form less extensive hydrogen bonds with water.
- For acyl chlorides, we do not mention solubility as it is very reactive in water.

3 Reactions

- Much of the chemistry of the acid derivatives involves the **conversion** from one into another, and into the parent carboxylic acid.
- These reactions typically proceed via **nucleophilic (acyl) substitution** at the carbonyl C atom.
- This type of reaction occurs readily because of the δ+ on the carbonyl C atom, which attracts nucleophiles and the presence of good leaving group **Y**.



The **Y** group is replaced by a nucleophile **:Z**, where **Y** = OH (carboxylic acid), OR' (ester), C*l* (acyl chloride), NH_2 (amide).

3.1 Esters

- Many esters occur naturally. Those of low molecular weight are fairly volatile, and many have pleasant odours.
- Esters often form a significant fraction of the fragrant oils of fruits and flowers. Hence, they are widely used in the food and perfumery industries.

🔍 **Fun Fact:** Simple esters such as 3–methylbutylethanoate can be used to give 'artificial' fruit–like aromas (banana in this case) in food. Natural aromas are usually far more complex. The natural aroma of an orange, for example, was found to contain 30 different esters, 10 carboxylic acids, 34 alcohols, 34 aldehydes and ketones, and 36 hydrocarbons!

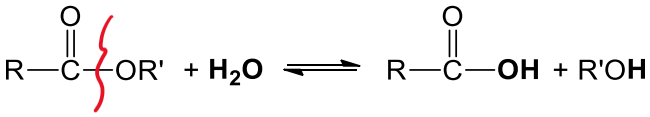
3.1.1 Hydrolysis

Students should be able to
h) Describe the acid and base hydrolysis of esters

- The hydrolysis of esters by boiling with water alone occurs very slowly. This hydrolysis can be sped up by heating under reflux with aqueous acid or alkali.

Acid hydrolysis of ester to form carboxylic acid

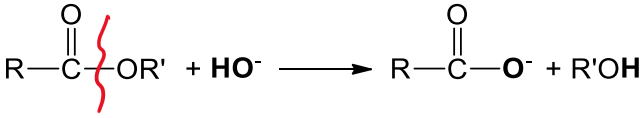
Reagents and conditions: **H_2SO_4(aq), heat**



*Acid hydrolysis is **reversible**.*

Base hydrolysis of ester to form carboxylate salt

Reagents and conditions: **NaOH(aq), heat**



During base hydrolysis, the carboxylic acid is obtained as its **salt**. The reaction is essentially **irreversible**, since a resonance–stabilised carboxylate anion shows little tendency to react with an alcohol.

🔍 **Fun Fact:** Alkaline hydrolysis is often referred to as saponification (derived from the French word 'sapon', meaning soap). Soap is made by the base hydrolysis of fats and oils.

3.2 Acyl Chlorides

- Acyl chlorides are usually liquids that fume in moist air. Acyl chlorides are extremely reactive and open to attack by nucleophiles.

3.2.1 Hydrolysis

Students should be able to

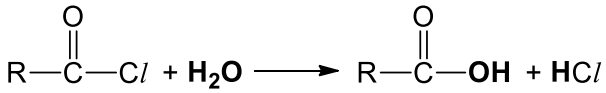
d) describe the hydrolysis of acyl chlorides

f) explain the relative ease of hydrolysis of acyl chlorides, alkyl chlorides and aryl chlorides

Hydrolysis of acyl chloride to carboxylic acid

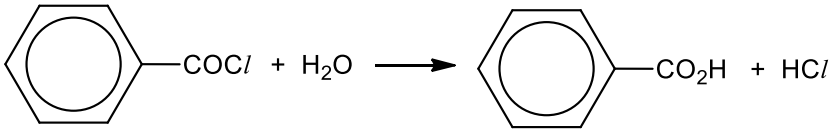
Type of reaction: **Hydrolysis**

Reagents and conditions: **H_2O**



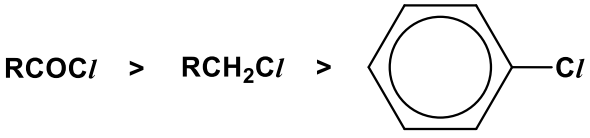
- Acyl chlorides are hydrolysed on contact with **water** at **room temperature**, giving white fumes of hydrogen chloride.
- With cold water, ethanoyl chloride **reacts vigorously** but benzoyl chloride reacts only **slowly**.

$CH_3COCl + H_2O \rightarrow CH_3CO_2H + HCl$



Note: This is a nucleophilic substitution reaction where water is the nucleophile. It is better known as hydrolysis to be more specific.

- **Ease of Hydrolysis:**



- In RCOC*l* (acyl chloride), the carbonyl C atom is **highly electron deficient** due to the **electron-withdrawing inductive effect** of the highly electronegative O atom, together with the C*l* atom, making it more susceptible to nucleophilic attack than RCH_2Cl (alkyl chloride) and C_6H_5Cl (aryl chloride).

- **Steric** factors affect ease of nucleophilic attack at the electron deficient C atom.
    - RCH_2Cl (sp^3 hybridised C, tetrahedral) experiences more steric hindrance than RCOCl (sp^2 hybridised C, trigonal planar). This reduces the chance of nucleophilic attack on the electron-deficient C in RCH_2Cl.

RCOCl	RCH_2Cl	C_6H_5Cl
C–Cl highly polarised	C–Cl less polarised	C–Cl partial double bond character
sp^2 hybridised C (trigonal planar)	sp^3 hybridised C (tetrahedral)	sp^2 hybridised C (trigonal planar)
least steric hindrance	higher steric hindrance than sp^2 hybridised C	steric hindrance from benzene ring

    - The relative ease of hydrolysis can be demonstrated by using $AgNO_3$(aq).

RCOCl	White ppt of AgCl forms ***immediately*** in cold water.
RCH_2Cl	No ppt in cold water. Some white ppt of AgCl forms on **warming**.
C_6H_5Cl	No ppt of AgCl even after prolonged boiling.

3.2.2 Condensation with Alcohols and Phenols to form Esters

Students should be able to

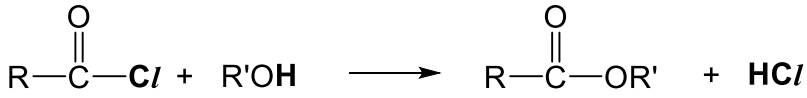
e) Describe the condensation reactions of acyl chlorides with alcohols, phenols and primary amines

g) Describe the formation of esters from the condensation reaction of acyl chlorides, using phenyl benzoate as an example

Condensation of acyl chloride with alcohols to form ester

Type of reaction: **Condensation**

Reagents and conditions: **R'OH** *(heat is not required)*

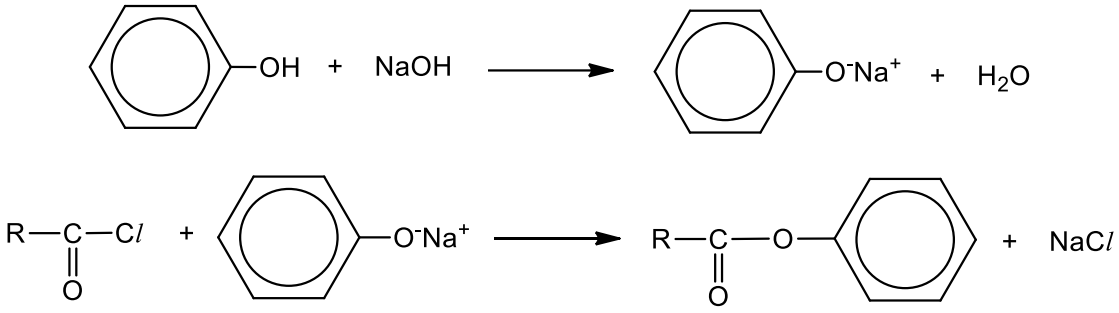


- The reaction is **irreversible** (compared to the reversible reaction between RCO_2H and R'OH) since acyl chlorides are good acylating agents and Cl^- is a better leaving group than OH^-.
- In addition, the HCl formed is gaseous and is removed from the system immediately upon forming, thereby driving the reaction to completion.

Condensation of acyl chloride with phenol to form ester

Type of reaction: **Condensation**

Reagents and conditions: **C_6H_5OH and NaOH(aq)**



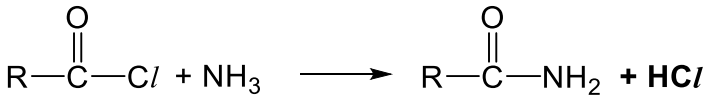
- Phenol can react with acyl chlorides to form phenyl esters. NaOH(aq) is first added to form the **stronger nucleophile**, **$C_6H_5O^-$**, before substitution is carried out.

3.2.3 Condensation with Ammonia and Amines to form Amides

Condensation of acyl chloride with ammonia to form primary amide

Type of reaction: **Condensation**

Reagents and conditions: **NH_3** *(heat is not required)*



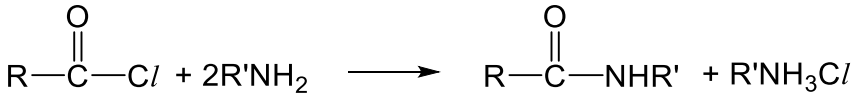
- The HC*l*(g) formed will immediately react with excess NH_3 to give NH_4Cl.

$$RCOCl + 2NH_3 \rightarrow RCONH_2 + NH_4Cl$$

Condensation of acyl chloride with amine to form amide

Type of reaction: **Condensation**

Reagents and conditions: **$R'NH_2$** *(heat is not required)*



Worked Example 5

Name the acyl chlorides used to prepare the following compounds.

(i) $CH_3CH_2CH_2CO_2H$ Answer:

(ii) $CH_3CH_2CO_2CH_3$ Answer:

(iii) $C_6H_5CONHCH_3$ Answer:

Worked Example 6 (N04/I/27)

Which compound reacts with each of

- cold NaOH(aq);
- CH_3OH, heat under reflux with concentrated H_2SO_4;
- PCl_5?

A $ClCOCOCl$
B $ClCOCO_2CH_3$
C $HOCH_2CO_2CH_3$
D HO_2CCO_2H

Answer:

You are now ready to attempt Tutorial Questions 5 to 8.

4 Summary of Reactions of Acid Derivatives