RAFFLES INSTITUTION
YEAR 6 H2 CHEMISTRY 2025
Lecture Notes 19 – Carboxylic Acids & Derivatives

A Content

I Carboxylic acids (exemplified by ethanoic acid and benzoic acid)
  - (i) Formation from primary alcohols and nitriles
  - (ii) Salt, ester and acyl chloride formation

II Acyl chlorides (exemplified by ethanoyl chloride)
  - (i) Ease of hydrolysis compared with alkyl and aryl chlorides
  - (ii) Reaction with alcohols, phenols and primary amines

III Esters (exemplified by ethyl ethanoate and phenyl benzoate)
  - (i) Formation from carboxylic acids and from acyl chlorides
  - (ii) Hydrolysis (under acidic and under basic conditions)

B Learning outcomes

Candidates 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

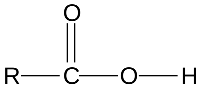
(c) explain the acidity of carboxylic acids and of chlorine-substituted ethanoic acids in terms of their structures
(d) describe the hydrolysis of acyl chlorides
(e) describe the condensation reactions of acyl chlorides with alcohols, phenols and primary amines
(f) explain the relative ease of hydrolysis 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 hydrolyses of esters

C References and Websites

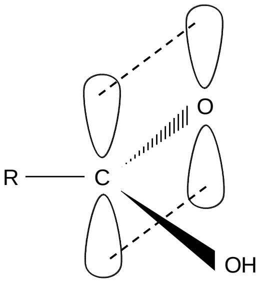
1 A-Level Chemistry (by Ramsden)
2 Organic Chemistry (by David Klein)
3 www.chemguide.co.uk

1 CARBOXYLIC ACIDS

1.1 Structure

Carboxylic acids may be represented as RCOOH,  $R-\overset{\overset{O}{\|}}{C}-O-H$, where R is H or alkyl or aryl group.

The functional group of carboxylic acids: **carboxyl group (−COOH)**. The name is a combination of the ***carbo***nyl and the hydro***xyl*** groups.



Carboxyl carbon atom is sp^2 hybridised

- 3 x sp^2 hybrid orbitals form σ bonds with the 2 oxygen atoms and the C atom of the R group or H atom.
- 1 x unhybridised p-orbital forms a π bond with the p-orbital of O atom of the C=O

The molecule is trigonal planar with respect to the carboxyl carbon.

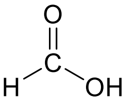
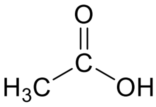
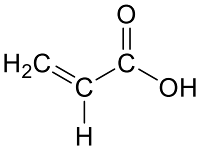
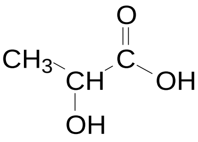
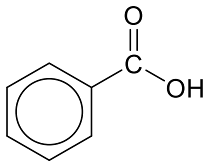
1.2 Nomenclature

Carboxylic acids are named by taking the name of the appropriate hydrocarbon, dropping the *–e* and adding the suffix *–oic acid*.

- ➢ The longest chain bearing the carboxyl group is considered the parent structure.
- ➢ **Numbering of the carbon chain starts from the <u>carboxyl carbon</u>** (principal functional group).
- ➢ When two carboxyl groups are present, the suffix *–dioic* acid is used.

e.g.		
	HOOC–COOH	ethanedioic acid
	$HOOCCH_2COOH$	propanedioic acid

Examples:

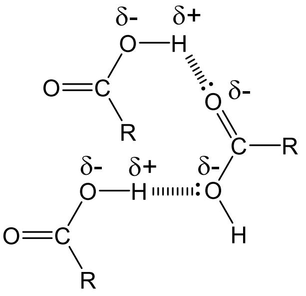
 methanoic acid (formic acid)	 ethanoic acid (acetic acid)	 propenoic acid (acrylic acid)
 2-hydroxypropanoic acid (lactic acid)	 benzenecarboxylic acid (benzoic acid)	HO_2C-CO_2H ethanedioic acid (oxalic acid)

1.3 Physical Properties

1.3.1 Volatility

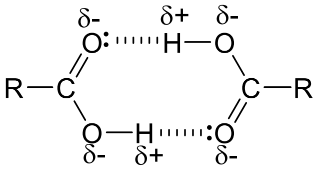
Comparison with compounds of other homologous series

- Carboxylic acids have **higher boiling points** than the corresponding alkanes and alcohols of similar size of electron cloud.

Compound	***M*r**	**Boiling point / °C**	**Reason**
$CH_3CH_2CH_2CH_3$	58	–0.5	Boiling point: $CH_3COOH > CH_3CH_2CH_2CH_3$ The hydrogen bonds between ethanoic acid molecules are stronger and require more energy to break compared to the instantaneous dipole-induced dipole interactions between butane molecules.  Intermolecular hydrogen bonding for a generic acid.
CH_3COOH	60	118	

Compound	***M*r**	**Boiling point / °C**	**Reason**
$CH_3CH_2CH_2OH$	60	97	Boiling point: $CH_3COOH > CH_3CH_2CH_2OH$ Both ethanol and ethanoic acid are capable of forming intermolecular hydrogen bonds. The hydrogen bonds between ethanoic acid molecules are stronger and require more energy to break because the **–OH group in ethanoic acid is more polarised** due to the presence of the **electron-withdrawing C=O group**.
CH_3COOH	60	118	

- Carboxylic acid molecules **dimerise** in the vapour state and in non-polar solvents, forming two hydrogen bonds between each pair of molecules.



The two intermolecular hydrogen bonds are formed between the carboxyl oxygen atom of one molecule and the hydroxyl hydrogen atom of another molecule.

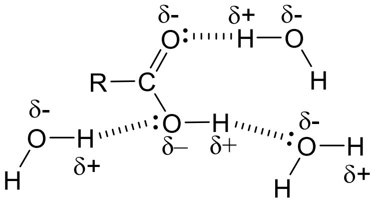
This accounts for the observation that the relative molecular mass of ethanoic acid when dissolved in benzene is approximately 120, but is 60 when dissolved in water.

Comparison within the homologous series

Compound	**Boiling point / °C**	**Reason**
$HCOOH$	101	The boiling point increases with increasing length of alkyl chain of the carboxylic acids due to an **increase in electron cloud size** and the **polarisability of the electron cloud** of each carboxylic acid, leading to **stronger instantaneous dipole-induced dipole interactions** between molecules.
CH_3COOH	118	
CH_3CH_2COOH	141	
$CH_3CH_2CH_2COOH$	164	

1.3.2 Solubility

- The first four members of the aliphatic acids are completely miscible with water because of:

1.	the ability of the –COOH group to form **<u>hydrogen bonds</u>** with water molecules. 
2.	the partial dissociation of carboxylic acids in water to form **<u>ions, i.e. H_3O^+ and $RCOO^-$</u>**, which are capable of forming **ion-dipole interactions** with water molecules. $RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$

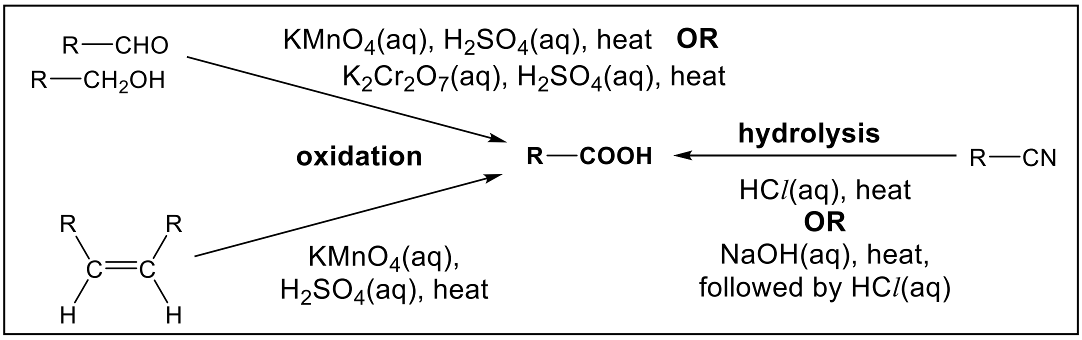
- As the **length of the non-polar hydrocarbon chain increases**, **<u>solubility in water decreases</u>**.
- Benzoic acid dissolves readily in hot water but forms a white crystalline solid when cooled as it is only slightly soluble in cold water.

1.4 Preparation of carboxylic acids

Candidates should be able to describe the formation of carboxylic acids from alcohols, aldehydes and nitriles.

Carboxylic acids may be prepared in a number of ways, namely

(a) **hydrolysis**
(b) **oxidation**



1.4.1 Hydrolysis of nitriles

	Reagents & conditions	Balanced equations
Acidic hydrolysis	HC*l*(aq), heat **or** H_2SO_4(aq), heat	$R{-}C{\equiv}N + 2H_2O + H^+ \xrightarrow[heat]{} R{-}COOH + NH_4^+$
Alkaline hydrolysis	NaOH(aq), heat, followed by acidification with HC*l*(aq), room temperature	$R{-}C{\equiv}N + H_2O + OH^- \xrightarrow[heat]{} R{-}COO^- + NH_3$ $\downarrow H^+$ $R{-}COOH + NH_4^+$

1.4.2 Hydrolysis of acyl chlorides (refer to Section 2.3.1.1)

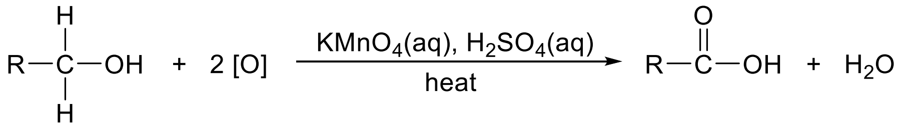
1.4.3 Hydrolysis of esters (refer to Section 2.3.2.1)

1.4.4 Hydrolysis of amides (refer to Organic Nitrogen Compounds notes)

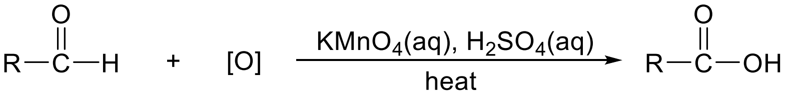
1.4.5 Oxidation of primary alcohols and aldehydes

Primary alcohols are oxidised via aldehydes to carboxylic acids.

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



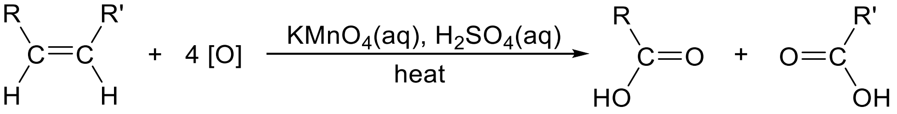
1° alcohols



aldehydes

1.4.6 Oxidative cleavage of alkenes

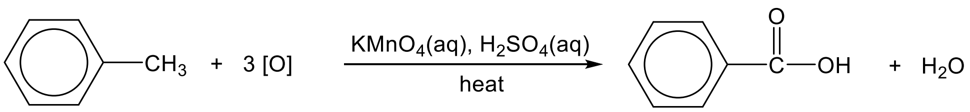
Reagents / conditions : **$KMnO_4$ (aq), H_2SO_4(aq), heat/heat under reflux** (**<u>will not work</u>** with $K_2Cr_2O_7$ (aq), H_2SO_4 (aq), heat)

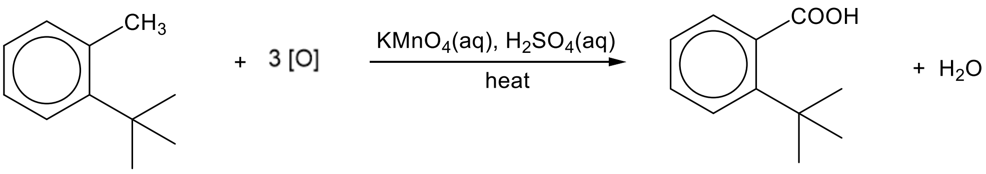


Example: $CH_3CH{=}CHCH_3 + 4[O] \xrightarrow{KMnO_4\,(aq),\ H_2SO_4\,(aq),\ heat} 2CH_3COOH$

1.4.7 Side-chain oxidation of an alkylbenzene to form benzoic acid

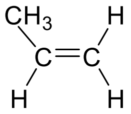
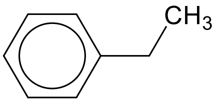
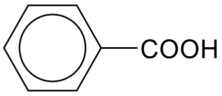
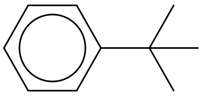
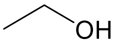
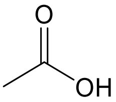
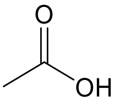
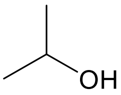
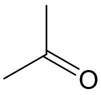
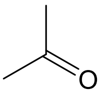
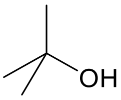
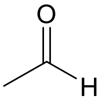
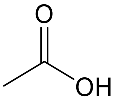
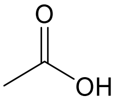
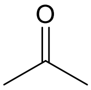
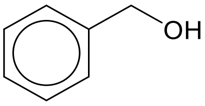
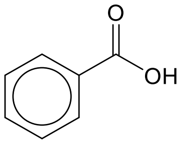
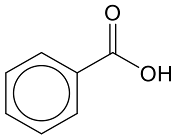
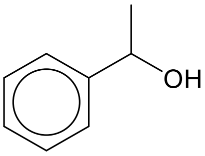
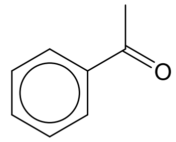
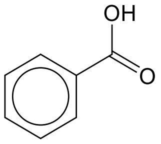
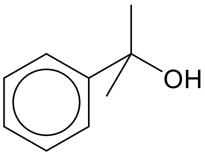
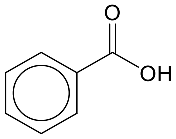
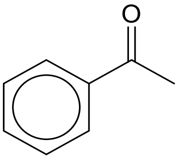
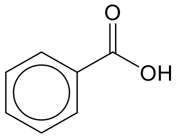
Reagents / conditions : **$KMnO_4$ (aq), H_2SO_4(aq), heat/heat under reflux** (**<u>will not work</u>** with $K_2Cr_2O_7$ (aq), H_2SO_4 (aq), heat)





1.4.8 Comparison of oxidation by hot acidified $KMnO_4$ and $K_2Cr_2O_7$

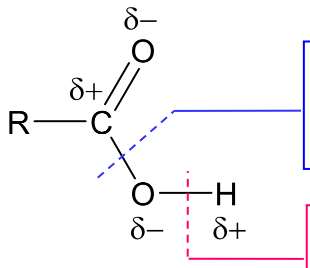
$KMnO_4$ and $K_2Cr_2O_7$ do not have the same oxidising abilities even under the same conditions. It is also important to take note of how the **different benzene side chains** react when subjected to strong oxidation. (Note: NR = No reaction)

			$K_2Cr_2O_7$(aq), H_2SO_4(aq), heat	**$KMnO_4$(aq), H_2SO_4(aq), heat**
Alkene			NR	$CH_3COOH + CO_2 + H_2O$
Alkylbenzene			NR	 + CO_2 + H_2O
			NR	NR
1° alcohols				
2° alcohols				
3° alcohols			NR	NR
Aldehyde				
Ketones			NR	NR
Directly attached to benzene ring	1° alcohols			
	2° alcohols			
	3° alcohols		NR	
	Ketones		NR	

1.5 Reactions of carboxylic acids

Candidates should be able to 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.

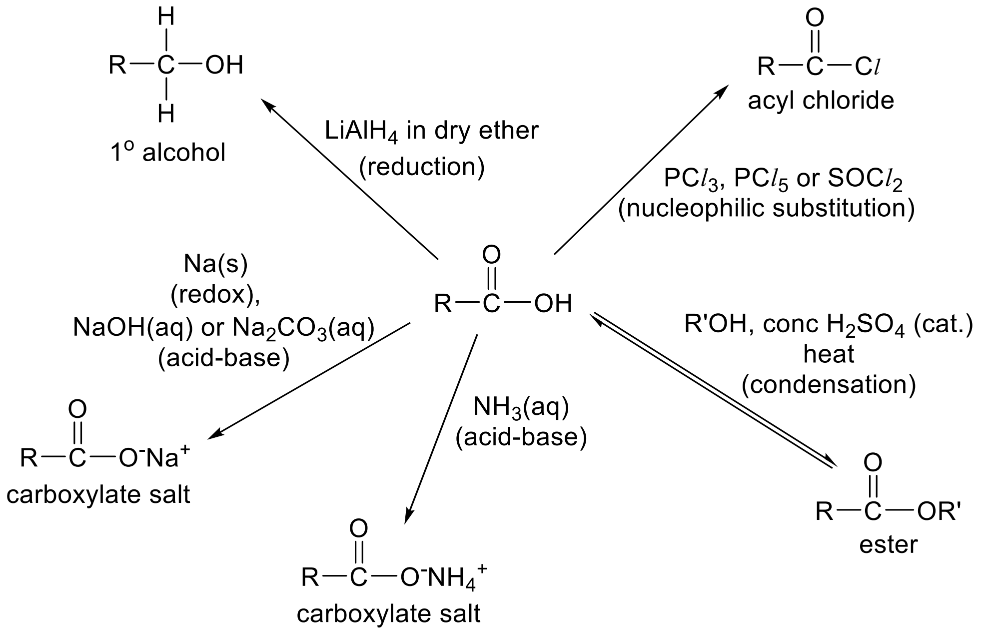
We can identify two main reactive centres from the general structure of a carboxylic acid.



The **C–O bond**, which may break heterolytically during the substitution of the –OH group. Alcohols take part in similar reactions.

The O–H bond which breaks heterolytically, releasing a proton. This accounts for the **acidic character** of the carboxyl group which allows the **formation of ionic salts**. A similar process occurs in alcohols and phenols.

Reactions of carboxylic acids



Carboxylic acids are generally **stable to oxidation** except for **methanoic acid** and **ethanedioic acid**.

Methanoic acid **HCOOH**	Reagents / conditions : **Tollens' reagent** or **Fehling's solution (followed by acidification),** **$KMnO_4$(aq), H_2SO_4(aq), heat** or **$K_2Cr_2O_7$(aq), H_2SO_4(aq), heat** Equation : $HCO_2H + [O] \rightarrow CO_2 + H_2O$
Ethanedioic acid **HOOC–COOH**	Reagents / conditions : **$KMnO_4$ (aq), H_2SO_4 (aq), heat** Equation : $HOOC–COOH + [O] \rightarrow 2CO_2 + H_2O$

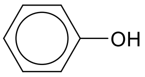
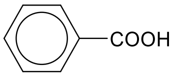
1.5.1 Fission of the O–H bond: Acidity

Candidates should be able to explain the acidity of carboxylic acids and of chlorine-substituted ethanoic acids in terms of their structures.

Carboxylic acids are weak acids as they dissociate only partially in water.

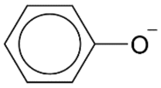
$$\underset{\text{weak acid}}{RCOOH} \rightleftharpoons \underset{\text{carboxylate}}{RCOO^-} + H^+$$

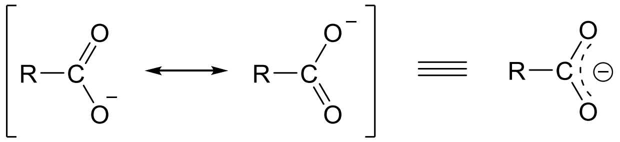
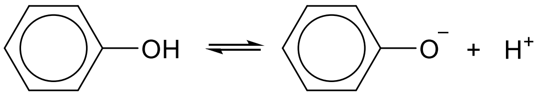
(A) Comparison of the acid strengths of compounds containing –OH group

Compound	CH_3CH_2OH	H_2O		CH_3COOH		$ClCH_2COOH$
K_a / mol dm^{-3}	1.3×10^{-16}	1.0×10^{-14}	1.0×10^{-10}	1.7×10^{-5}	6.3×10^{-5}	1.4×10^{-3}

Acidity: Alcohols < Water < Phenols < Carboxylic acids

The relative acidities may be explained in terms of the **stability of the conjugate base formed** upon dissociation of the acid in water. **The more stable the conjugate base, the stronger the acid.** In this case, the relative stabilities of the conjugate bases decrease in this order:

$RCOO^-$ >  > **RO^-**

Carboxylic acid	$RCOOH \rightleftharpoons RCOO^- + H^+$ ➢ $RCOO^-$ has 2 equivalent resonance structures with **delocalisation of the negative charge over 2 highly electronegative O atoms**. ➢ This results in the carboxylate anion being **greatly stabilised** compared to phenoxide and alkoxide ions.  2 equivalent resonance structures resonance hybrid Note: As a result of the resonance, the 2 C–O bonds are equal in length. The negative charge is also equally distributed between the 2 oxygen atoms.
Phenol	 ➢ In the phenoxide ion, the p-orbital containing the **lone pair** of electrons on the O atom **overlaps** with the π-electron cloud of the benzene ring so that the **negative charge on O delocalises into the benzene ring**. ➢ This resonance stabilisation is **not as great as that in the $RCOO^-$ ion** in which the negative charge is delocalised over 2 highly electronegative O atoms. ➢ The **dispersal** of negative charge **stabilises** the phenoxide ion so that it is more stable than the alkoxide ion.
Alcohol	$ROH \rightleftharpoons RO^- + H^+$ ➢ In RO^-, the electron-donating alkyl group **intensifies** the negative charge on O atom. ➢ Charge on RO^- ion also remains **localised** on a single electronegative O. ➢ The alkoxide ion is, therefore, the **least stable**. ➢ Hence, alcohols are the **least acidic**.

(B) Effect of substituents on acidity

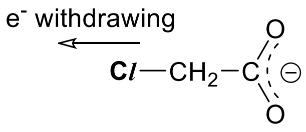
The strength of the carboxylic acid RCOOH depends on the following factors:

(I) Nature of R group

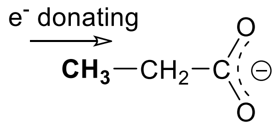
Electron-donating substituents	Electron-withdrawing substituents
Example: alkyl groups	**Example**: F, C*l* atoms
➢ **intensify** the negative charge on the carboxylate anion ➢ **destabilises** the conjugate base of the acid ➢ **decreases** acidity.	➢ **disperse** the negative charge on the carboxylate anion. ➢ **stabilises** the conjugate base of the acid. ➢ **increases** acidity.

Example:

C*l*–CH_2COOH (pK_a = 2.86) is a stronger acid than **CH_3**–CH_2COOH (pK_a = 4.87).



C*l* is e⁻ withdrawing, disperses negative charge on –COO^-, stabilises anion, increases acidity



CH_3 is e⁻ donating, intensifies negative charge on –COO^-, destabilises anion, decreases acidity

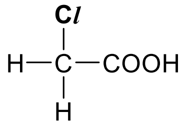
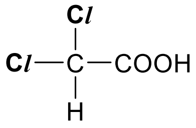
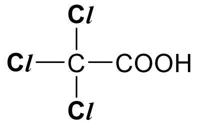
(II) Number of substituents on R group

The acid strength of the carboxylic acid also depends on the **number** of electron-withdrawing (or electron-donating) substituents next to the –COOH group.

The **greater** the number of **electron-withdrawing** substituent groups, the **greater the extent of negative charge dispersal on $RCOO^-$**. The conjugate base, $RCOO^-$, is **stabilised** and the acid, RCOOH, is **more acidic.**

The **greater** the number of **electron-donating** groups, the **more intensified the negative charge on $RCOO^-$**. The conjugate base, $RCOO^-$, is **destabilised** and the acid, RCOOH, is **less acidic.**

Example:

Formula	 $ClCH_2COOH$	 $Cl_2CHCOOH$	 Cl_3CCOOH
pK_a	2.86	1.29	0.65 (most acidic)

C*l*$_3$CCOOH (pK_a = 0.65) is a stronger acid than C*l*CH_2COOH (pK_a = 2.86).

Conversely, the **greater** the number of **electron-donating** groups, the **more intensified the negative charge on $RCOO^-$.** The conjugate base, $RCOO^-$, is **destabilised** and the acid, RCOOH, is **less acidic**.

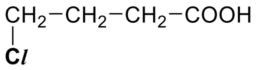
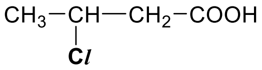
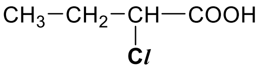
(III) Positions of substituents on R group

The strength of the carboxylic acid also depends on the **position** of electron-withdrawing substituents in the vicinity of the –COOH group.

Inductive effects operate through σ bonds and are dependent on **distance**, the effect of the electron-withdrawing substituents **decreases as the substituent moves further from the –COOH group**.

The **closer** the electron-withdrawing substituents are to the –COOH, the **more** acidic the carboxylic acid.

Example:

Formula	 $\underset{Cl}{CH_2}-CH_2-CH_2-COOH$	 $CH_3-\underset{Cl}{CH}-CH_2-COOH$	 $CH_3-CH_2-\underset{Cl}{CH}-COOH$
p*K*a	4.52	4.05	2.86 (most acidic)

CH_3-CH_2-CH**C*l***-COOH (pK_a = 2.86) is a stronger acid than CH_2**C*l***-CH_2-CH_2-COOH (pK_a = 4.52).

The electron withdrawing –C*l* is closer to the $–COO^–$ group in CH_3CH_2CH**C*l***$COO^–$ than in CH_2**C*l***$CH_2CH_2COO^–$, dispersing the negative charge on CH_3CH_2CH**C*l***$COO^–$ to a greater extent, causing CH_3CH_2CH**C*l***COOH to be a stronger acid.

Exercise:

Which of the following sequences ranks the compounds in increasing order of pK_a?

A $C_6H_5OH < C_2H_5OH < CCl_3CO_2H < CH_3CO_2H$

B $C_6H_5OH < C_2H_5OH < CH_3CO_2H < CCl_3CO_2H$

C $CCl_3CO_2H < CH_3CO_2H < C_6H_5OH < C_2H_5OH$

D $CCl_3CO_2H < CH_3CO_2H < C_2H_5OH < C_6H_5OH$

1.5.2 Fission of the O–H bond: Salt formation

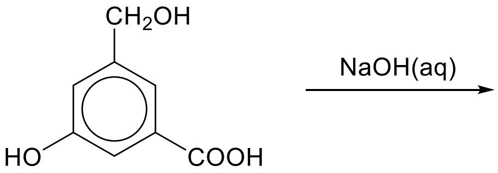
Due to its ability to act as an acid, carboxylic acids react with **metals, alkalis, carbonates and hydrogen carbonates** and **aqueous NH_3** to form salts.

Reaction With	**Alcohols, ROH**	**Phenol, C_6H_5OH**	**Carboxylic acid, RCOOH**
Na(s)	Redox reaction with effervescence of hydrogen: ROH + Na $\longrightarrow RO^-Na^+ + \frac{1}{2}H_2$	Vigorous redox reaction with evolution of hydrogen: $C_6H_5OH + Na$ $\longrightarrow C_6H_5O^-Na^+ + \frac{1}{2}H_2$	Explosive redox reaction with evolution of hydrogen: RCOOH + Na(s) $\longrightarrow RCOO^-Na^+ + \frac{1}{2}H_2$
NaOH(aq)	**No reaction**. Alcohol is not acidic enough to react with the reagent.	Acid-base reaction and phenol dissolves: $C_6H_5OH + NaOH$ $\rightarrow C_6H_5O^-Na^+ + H_2O$	Acid-base reaction: RCOOH + NaOH $\rightarrow RCOO^-Na^+ + H_2O$
Na_2CO_3(aq)		**No reaction**. Phenol is not acidic enough to react with the reagent	Acid-base reaction with evolution of CO_2: $2RCOOH + Na_2CO_3$ $\rightarrow 2RCOO^-Na^+ + H_2O + CO_2$

Reaction With	**Alcohols, ROH**	**Phenol, C_6H_5OH**	**Carboxylic acid, RCOOH**
$NaHCO_3(aq)$	**No reaction.** Alcohol is not acidic enough to react with the reagent.	**No reaction.** Phenol is not acidic enough to react with the reagent.	Acid-base reaction with evolution of CO_2: $RCOOH + NaHCO_3$ $\rightarrow RCOO^-Na^+ + H_2O + CO_2$
$NH_3(aq)$			Acid-base reaction: $RCOOH + NH_3 \rightarrow RCOO^-NH_4^+$

Exercise:

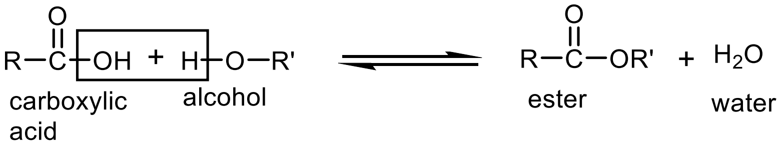
Give the structure of the organic product formed when an excess of NaOH(aq) is added to the following compound.



1.5.3 Fission of the C–O bond: Condensation

A carboxylic acid is converted into an ester when heated under reflux with an alcohol in the presence of an acid catalyst like concentrated sulfuric acid.

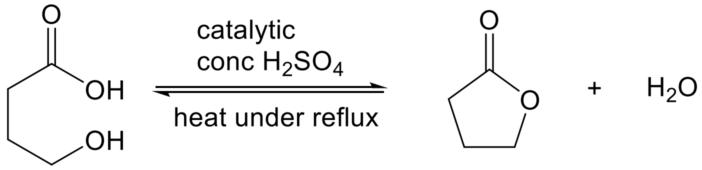
Reagents / conditions: **alcohol, catalytic conc H_2SO_4, heat/heat under reflux**



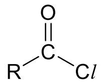
- The reaction is **reversible** (equilibrium constant is not very large, about 3.4)
- The equilibrium position is driven to the right by using
  - an excess of one of the reactants,
  - chemicals or special apparatus which remove water during the reaction.
- **Concentrated sulfuric acid is used as <u>catalyst</u>** to make the carboxyl carbon more electrophilic, hence increasing the rate of ester formation.

Examples:

$$CH_3COOH + HOCH_2CH_3 \xrightleftharpoons[\text{heat under reflux}]{\text{catalytic conc } H_2SO_4} CH_3COOCH_2CH_3 + H_2O$$



1.5.4 Fission of the C–O bond: Formation of acyl chlorides

A carboxylic acid is converted into an acyl chloride () using $\mathrm{PC}l_3$, $\mathrm{PC}l_5$ or $\mathrm{SOC}l_2$.

Reagents / conditions: **$\mathbf{PC}\boldsymbol{l}_\mathbf{3}$, $\mathbf{PC}\boldsymbol{l}_\mathbf{5}$ or $\mathbf{SOC}\boldsymbol{l}_\mathbf{2}$**

	RCOOH to RCOC*l*	**ROH to RC*l***
$\mathbf{PC}\boldsymbol{l}_\mathbf{3}$	$\mathrm{3RCOOH + PC}l_3 \rightarrow \mathrm{3RCOC}l + \mathrm{H_3PO_3}$	$\mathrm{3ROH + PC}l_3 \rightarrow \mathrm{3RC}l + \mathrm{H_3PO_3}$
$\mathbf{PC}\boldsymbol{l}_\mathbf{5}$	$\mathrm{RCOOH + PC}l_5 \rightarrow \mathrm{RCOC}l + \mathrm{POC}l_3 + \mathrm{HC}l$	$\mathrm{ROH + PC}l_5 \rightarrow \mathrm{RC}l + \mathrm{POC}l_3 + \mathrm{HC}l$
	Observation: White fumes of HC*l* observed.	
$\mathbf{SOC}\boldsymbol{l}_\mathbf{2}$	$\mathrm{RCOOH + SOC}l_2 \rightarrow \mathrm{RCOC}l + \mathrm{SO_2} + \mathrm{HC}l$	$\mathrm{ROH + SOC}l_2 \rightarrow \mathrm{RC}l + \mathrm{SO_2} + \mathrm{HC}l$
	Observation: White fumes of HC*l* observed.	

Note:

- None of the above reagents can be used to distinguish between a carboxylic acid and an alcohol because they give the same observations.
- The reaction with $\mathrm{SOC}l_2$ is convenient as the two other products are both gaseous and are easily removed from the reaction mixture.
- HC*l* does not form acyl chlorides with carboxylic acids.

1.5.5 Reduction to alcohols

Candidates should be able to describe the reactions of carboxylic acids in the formation of primary alcohols, via reduction with lithium aluminium hydride, using ethanol as an example.

Carboxylic acids can be **reduced to primary alcohols** by using lithium aluminium hydride, $\mathrm{LiA}l\mathrm{H_4}$ in dry ether. This **cannot be achieved** using sodium borohydride ($\mathrm{NaBH_4}$), or by heating with $\mathrm{H_2}$ and Ni.

Reagents / conditions : **$\mathbf{LiAlH_4}$ in dry ether**

$$\mathrm{RCOOH} \quad + \quad 4[\mathrm{H}] \xrightarrow{\mathrm{LiA}l\mathrm{H_4\ in\ dry\ ether}} \mathrm{RCH_2OH} \quad + \quad \mathrm{H_2O}$$

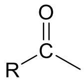
1.5.6 Distinguishing test for carboxylic acids

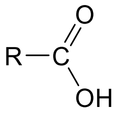
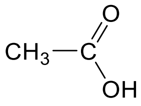
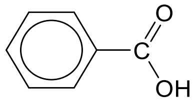
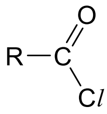
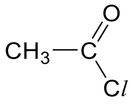
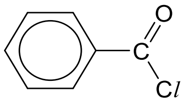
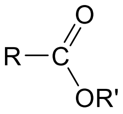
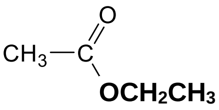
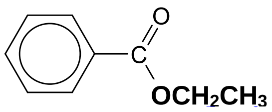
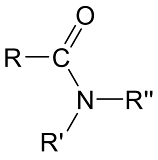
Test:	Add $\mathrm{Na_2CO_3(aq)}$ (or $\mathrm{NaHCO_3(aq)}$) at room temperature.
Observation:	Effervescence of $\mathrm{CO_2}$ gas which forms a white precipitate when bubbled into limewater.

2 CARBOXYLIC ACID DERIVATIVES

2.1 Structure and Nomenclature

Acid derivatives are formed when the –OH portion of the carboxyl group is replaced by another functional group (which usually includes an electronegative atom).

These derivatives all contain the acyl group,  .

	General structure	Examples	Nomenclature
Carboxylic acid		 ethanoic acid  benzoic acid	--
Acyl chloride (under the family of acyl halides)		 ethano**yl** **chloride**  benzo**yl** **chloride**	change –*ic* acid to –*yl chloride*
Ester		 **ethyl** ethanoate  **ethyl** benzoate	change –*ic* acid to –*ate.* *Name is preceded by alcohol.*
Amide		To be covered in *Organic Nitrogen Compounds*	

2.2 Physical Properties

2.2.1 Volatility

Acyl chlorides and esters have **lower** boiling points than the **parent carboxylic acids** as a result of their inability to **form intermolecular hydrogen bonds with their own molecules,** as they lack a H atom attached to a highly electronegative O atom.

Their predominant intermolecular forces are **permanent dipole-permanent dipole** interactions, which are weaker than the intermolecular hydrogen bonding between RCOOH molecules.

Acyl chlorides of lower M_r possess a sharp pungent smell and have an irritating effect on the eyes and mucous membrane, partly due to their **rapid hydrolysis in air to form HC*l* and carboxylic acids** (see section 2.3.1.1).

Volatile esters have strong, pleasant and fruity odours.

2.2.2 Solubility

Solubilities of carboxylic acid derivatives are dependent on the **size of the hydrocarbon chain**. As the **length of the non-polar hydrocarbon chain increases**, solubility in water **decreases**.

Esters are generally **insoluble in polar solvents** but are **soluble in non-polar solvents**.

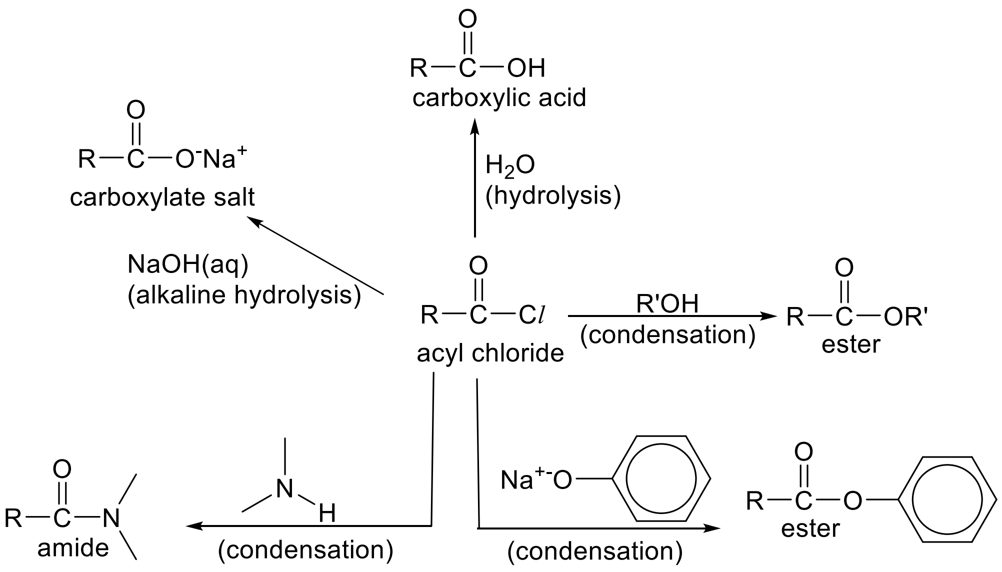
Acyl chlorides are **soluble in non-polar solvents** and **soluble in water**. They hydrolyse rapidly in water to form HC*l* and RCOOH, which then ionise (see section 2.3.1.1).

2.3 Reactions of Acid Derivatives

Acid derivatives, like carboxylic acids, contain the carboxyl group C=O, and the reactions of acid derivatives typically proceed via **condensation reaction** which involves the **attack of a nucleophile** at the **carboxyl carbon**.

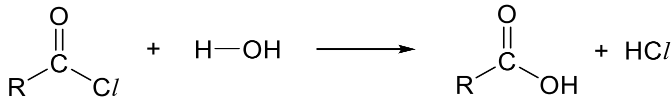
2.3.1 Reactions of acyl chlorides

Reactions of acyl chlorides



2.3.1.1 Hydrolysis of acyl chlorides

Candidates should be able to describe the hydrolysis of acyl chlorides.



$RCOCl + H-OH \longrightarrow RCOOH + HCl$

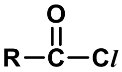
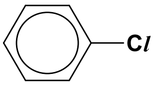
- Acyl chlorides are the most reactive of the derivatives of carboxylic acids.
- Acyl chlorides are hydrolysed on contact with water, even at room temperature.
- Heat and white fumes of HC*l* are evolved.
- Since HC*l* is very soluble in water, some remain dissolved in solution such that when RCOC*l* is reacted with water, the resultant solution is strongly acidic (pH ~ 1, due to complete ionisation of HC*l*).

Candidates should be able to explain the relative ease of hydrolysis of acyl chlorides, alkyl chlorides and aryl chlorides.

Relative ease of hydrolysis of acyl chlorides, alkyl chlorides and aryl chlorides

The ease of hydrolysis is dependent on two factors:

Electronic factors	**Steric factors**
Electron deficiency of C bonded to halogen	Presence of bulky substituent groups which hinder attack by nucleophile

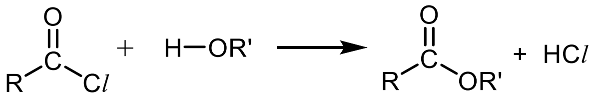
	 $R-\overset{\overset{O}{\parallel}}{C}-Cl$	**RCH_2Cl**	
Electronic factor	C=O carbon is bonded to **2 highly electronegative atoms**, O and Cl. ⇒ **higher δ+ charge** on C ⇒ **more susceptible** to attack by nucleophiles.	C–Cl carbon is bonded to only **1 highly electronegative atom**, Cl. ⇒ **lower δ+ charge** on C ⇒ **less susceptible** to attack by nucleophiles (as compared to $RCOCl$).	Overlapping of p–orbital on Cl atom with π-electron cloud of the benzene ring. This allows the lone pair of electrons in the p orbital of chlorine to delocalise into the π electron cloud of the benzene ring. ⇒ **C–Cl bond** has **partial double bond** character ⇒ no cleavage occurs due to strengthening of the C–Cl bond Electron-rich benzene ring **repels** nucleophile
Steric factor	**sp^2** hybridised C=O carbon ⇒ **less** steric hindrance since nucleophile attacks **trigonal planar** C	**sp^3** hybridised C–Cl carbon ⇒ **more** steric hindrance since nucleophile attacks **tetrahedral** C	--
Ease of hydrolysis	**$RCOCl > RCH_2\text{–}Cl > Ph\text{–}Cl$**		
Evidence: Reaction with aq. $AgNO_3$	White ppt of $AgCl$ is observed **immediately**.	No ppt. However, white ppt of $AgCl$ is observed only when **heated** with ethanolic $AgNO_3$.	No ppt even after prolonged boiling. No ppt is also observed when heated with ethanolic $AgNO_3$.

2.3.1.2 Reactions with alcohols, phenols, ammonia and amines

Candidates should be able to describe the
- condensation reactions of acyl chlorides with alcohols, phenols and primary amines.
- formation of esters from the condensation reactions of acyl chlorides, using phenyl benzoate as an example.

Acyl chlorides react with **alcohols** and **phenols** to form **esters**.

With alcohols:



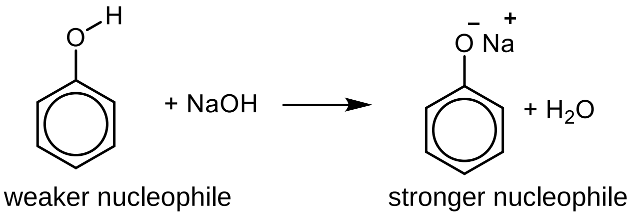
Compare with RCOOH,

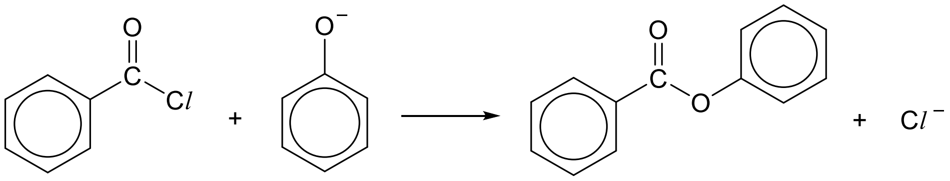
$$RCOOH + R'OH \underset{\text{heat}}{\overset{\text{catalytic conc } H_2SO_4}{\rightleftharpoons}} RCOOR' + H_2O$$

With phenols:

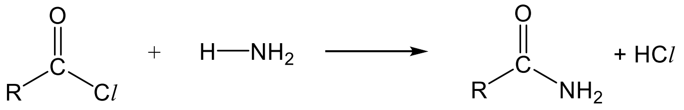
Phenols do not react with carboxylic acids to form esters and require the use of acyl chlorides instead.

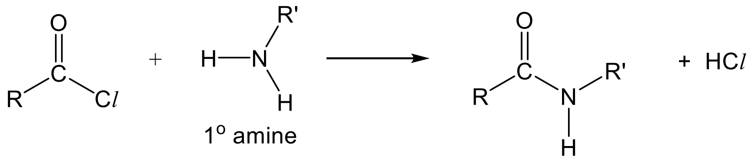
When preparing phenolic esters, it is advisable to first convert the **less nucleophilic phenol to a more nucleophilic phenoxide ion**.

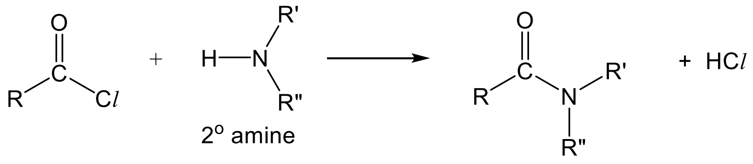


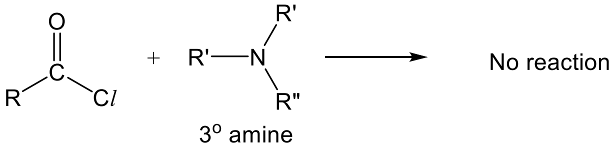


Acyl chlorides react with **ammonia** and **amines** (1^o and 2^o) to give **amides**.



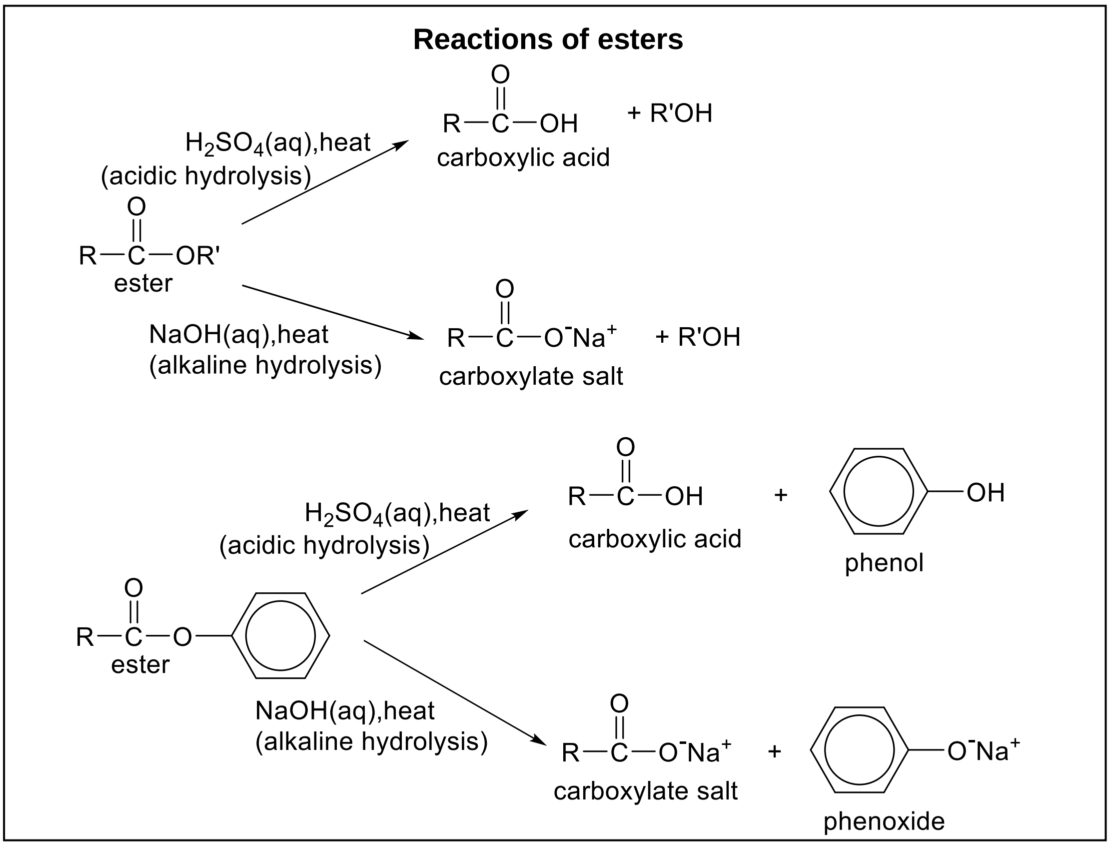






Note: **Tertiary** amines **do** not react with acyl chlorides.

2.3.2 Reactions of esters

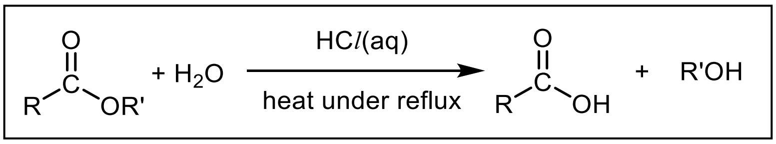


2.3.2.1 Hydrolysis of esters

Candidates should be able to describe the acid and base hydrolyses of esters.

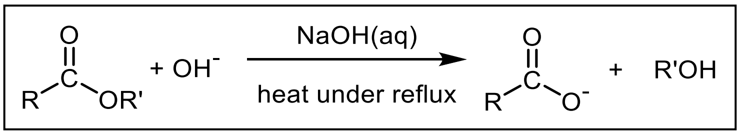
The hydrolysis of esters by heating with water alone occurs extremely slowly. This hydrolysis can be sped up by **heating under reflux with acid or alkali**.

(I) Acidic hydrolysis



In the acidic hydrolysis of ester, the nucleophile is H_2O.

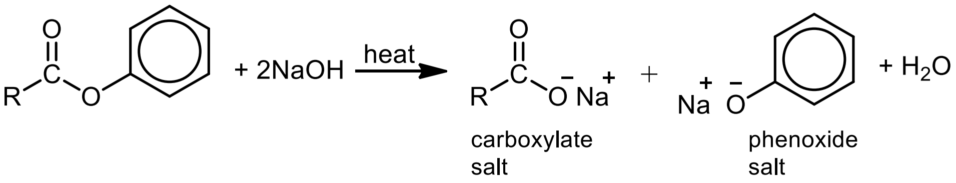
(II) Alkaline/Basic hydrolysis



In the alkaline hydrolysis of ester, the nucleophile is OH^- (stronger nucleophile than H_2O). Under alkaline conditions, the carboxylic acid is obtained as its salt. Alkaline hydrolysis is often referred to as *saponification*.

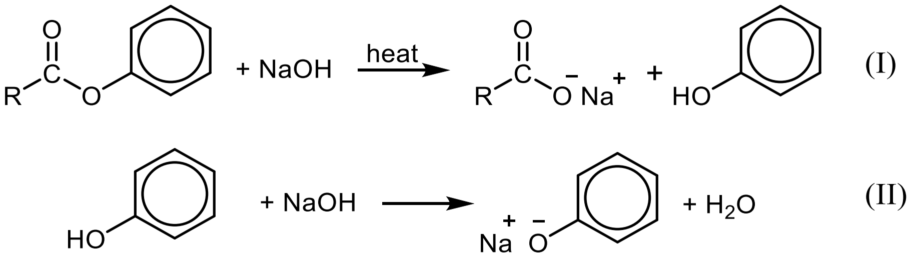
Note: If the hydroxy compound formed is a phenol or substituted phenol, then the phenoxide salt is obtained.

Example:



2 moles of NaOH(aq) is required for reaction with 1 mole of the above ester.

- 1 mole of NaOH(aq) is required for the hydrolysis of the ester linkage to form the carboxylate salt and phenol (as shown in (I) below).
- the other 1 mole of NaOH(aq) is required for the neutralisation of the acidic phenol (as shown in (II) below).



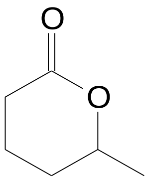
Exercise Questions:

1. Which of the following cannot be converted into CH_3CH_2COOH by either hydrolysis or oxidation?

A $CH_3CH_2COOCH_3$ ✓ hyd
B CH_3CH_2CHO ✓ ox
C $CH_3CH_2(CH_2)_2OH$
D CH_3CH_2COCl hyd

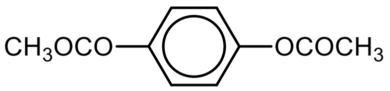
C

2. Draw the structure of the organic product formed.

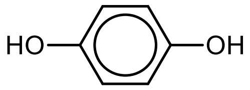


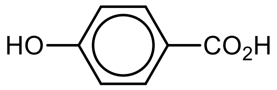
NaOH(aq)
⟶
heat under reflux

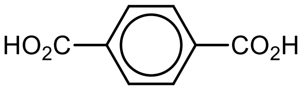
3. What are the products formed when compound **J** is heated with dilute sulfuric acid?

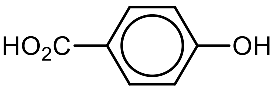


J

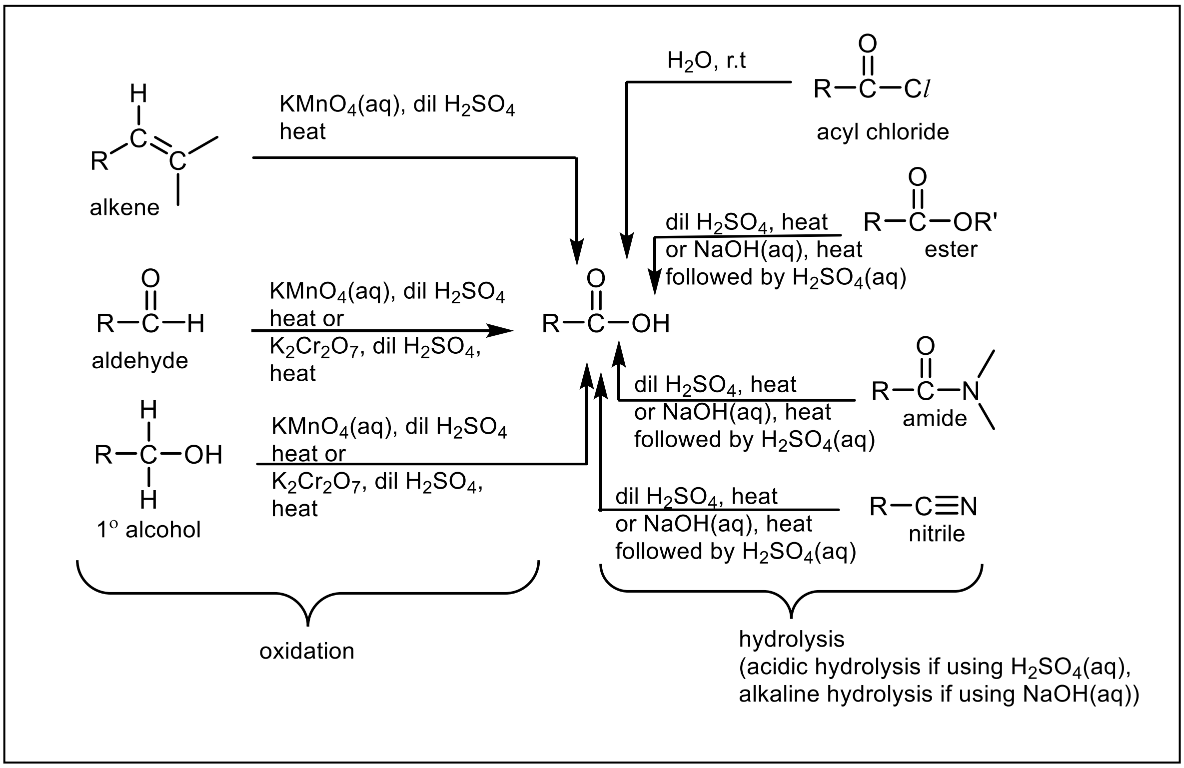
A  and CH_3CO_2H

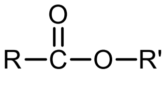
B  and CH_3OH

C CH_3CH_2OH,  and HCO_2H

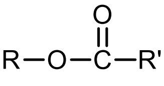
D CH_3OH,  and CH_3CO_2H

Summary of Carboxylic Acids & Derivatives

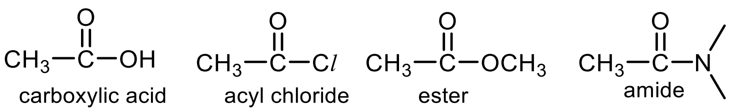


RCOOR' is 

$R-\overset{O}{\overset{\parallel}{C}}-O-R'$

ROCOR' is 

$R-O-\overset{O}{\overset{\parallel}{C}}-R'$



do not give undergo oxidation with I_2 and NaOH (iodoform test)