

RAFFLES INSTITUTION YEAR 6 H2 CHEMISTRY 2023 Lecture Notes 18 – Carboxylic Acids & Derivatives

A Content

- 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, aryl group.

The functional group of carboxylic acids: carboxyl group (-COOH). The name is a combination of the carbonyl and the hydroxyl groups.



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 HOOCCH₂COOH propanedioic acid

Examples:



1.3 **Physical Properties**

1.3.1 Volatility

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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	Mr	Boiling point / °C	Reason		
CH ₃ CH ₂ CH ₂ CH ₃	58	-0.5	Boiling point: $CH_3COOH > CH_3CH_2CH_2CH_3$ $\delta^- \delta^+$ The hydrogen bonds between $O-H$ ethanoic acid molecules are $O=C$ stronger and require more energy to break compared to the instantaneous dipole-induced dipole interactions $\delta^- \delta^+ \delta^-$		
СН₃СООН	60	118	between butane molecules. O=C H R Intermolecular hydrogen bonding for a generic acid.		

Compound	Mr	Boiling point / °C	Reason
			Boiling point: CH ₃ COOH > CH ₃ CH ₂ CH ₂ OH
CH ₃ CH ₂ CH ₂ OH	60	97	Both ethanol and ethanoic acid are capable of forming intermolecular hydrogen bonds.
CH₃COOH	60	118	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.

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



R-C C-R The two intermolecular hydrogen bond are formed between the carboxyl oxygen atom of one molecule and the hydroxyl hydrogen atom of another i The two intermolecular hydrogen bonds

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.

Compound	Boiling point / °C	Reason
HCOOH	101	The bailing point increases with increasing locally of the
CH₃COOH	118	chain of the carboxylic acids due to an increase in electron
CH₃CH₂COOH	141	cloud size and the polarisability of the electron cloud of each carboxylic acid, leading to stronger instantaneous
CH₃CH₂CH₂COOH	164	dipole-induced dipole interactions.

Comparison within the homologous series

1.3.2 Solubility

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



- As the length of the non-polar hydrocarbon chain increases, solubility in water decreases.
- 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/(aq), heat or H₂SO₄(aq), heat	$R-C\equiv N + 2H_{2}O + H^{+}$ heat $R-COOH + NH_{4}^{+}$		
Alkaline hydrolysis	NaOH(aq), heat, followed by acidification with HC/(aq), room temperature	$R-C\equiv N + H_{2}O + OH \xrightarrow{heat} R-COO^{-} + NH_{3}$ $\downarrow H^{+}$ $R-COOH + NH_{4}^{+}$		

- 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)

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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.



1.4.6 Oxidative cleavage of alkenes



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



1.4.8 Comparison of oxidation by hot acidified KMnO₄ and K₂Cr₂O₇

 $KMnO_4$ 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 ₂ Cr ₂ O ₇ (aq), H ₂ SO ₄ (aq), heat	KMnO₄(aq), H₂SO₄(aq), heat
A	lkene	CH3 H C=C H H	NR	CH₃COOH + CO₂ + H₂O
Alkylbenzene		CH3	NR	Соон + со2 + Н 20
			NR	NR
1° a	alcohols	∕∩он	ОН	ОН
2° a	alcohols	Н	, Lo	\downarrow_{\circ}
3° a	alcohols	Н	NR	NR
Aldehyde		O H	ОН	ОН
Ketones		o	NR	NR
ring	1° alcohols	О	ОН	ОН
to benzene	2° alcohols	ОН	Oto	OH
tly attached t	3° alcohols	ОН	NR	ОН
Direc	Ketones	O	NR	ОН

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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.





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), KMnO4(aq), H ₂ SO4(aq), heat or K ₂ Cr ₂ O ₇ (aq), H ₂ SO4(aq), heat			
	Equation	$: HCO_2H + [O] \rightarrow CO_2 + H_2O$		
Ethanedioic acid	Reagents / conditions	s : KMnO₄ (aq), H₂SO₄ (aq), heat		
HOUC-COOH	Equation	: HOOC-COOH + [O] \rightarrow 2CO ₂ + H ₂ O		

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.

 $\begin{array}{rcl} \mathsf{RCOOH} & \rightleftharpoons & \mathsf{RCOO}^- \ + & \mathsf{H}^* \\ \text{weak acid} & & \mathsf{carboxylate} \end{array}$

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

Compound	CH ₃ CH ₂ OH	H ₂ O	Ю-он	СН₃СООН	Соон	C/CH₂COOH
K _a / mol dm ⁻³	1.3 x 10 ⁻¹⁶	1.0 x 10 ⁻¹⁴	1.0 x 10 ⁻¹⁰	1.7 x 10⁻⁵	6.3 x 10 ⁻⁵	1.4 x 10 ⁻³



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:

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	$RCOO^- > \bigcirc -0 > RO^-$
	RCOOH ≈ RCOO ⁻ + H ⁺
Carboxylic acid	 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. R - C - O R - C - O 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 of O 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 the the star the released over the phenoxide ion.
	$ROH \rightleftharpoons RO^- + H^+$
Alcohol	 A 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

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Electron-donating substituents		Electron-withdrawing substituents		
Example: alkyl groups		Example: F, Cl atoms		
4	intensify the negative charge on the carboxylate anion	8	disperse the negative charge on the carboxylate anion.	
A	destabilises the conjugate base of the acid	8	stabilises the conjugate base of the acid.	
A	decreases acidity.	۶	increases acidity.	

Example:

CI-CH₂COOH ($pK_a = 2.86$) is a stronger acid than CH₃-CH₂COOH ($pK_a = 4.87$).

e ⁻ withdrawing C <i>I</i> −−CH ₂ −C(⊖ O	$ \begin{array}{c} e^{-} \text{ donating} \\ \hline CH_{3} - CH_{2} - C \\ O \\ \end{array} $
Cl is e ⁻ withdrawing, disperses	CH ₃ is e [−] donating, intensifies
negative charge on -COO ⁻ ,	negative charge on -COO ⁻ ,
stabilises anion, increases acidity	destabilises anion, decreases acidity

(II) Number of substituents on R group

The acid strength of the carboxylic acid also depends on the **number** of electronwithdrawing (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	С/ Н—С—СООН Н	С <i>і</i> с <i>і</i> —с—соон н	С/ С/—С—СООН С/
р <i>К</i> а	2.86	1.29	0.65 (most acidic)

 Cl_3CCOOH (pK_a = 0.65) is a stronger acid than C/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 electronwithdrawing 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	CH ₂ -CH ₂ -CH ₂ -COOH	СН ₃ -СН—СН ₂ -СООН	СН ₃ -СН ₂ -СН-СООН
	<i>Cl</i>	С <i>I</i>	С/
pK₄	4.52	4.05	2.86 (most acidic)

CH₃-CH₂-CHC*I*-COOH ($pK_a = 2.86$) is a stronger acid than CH₂C*I*-CH₂-CH₂-COOH ($pK_a = 4.52$).

The electron withdrawing -Cl is closer to the $-COO^-$ group in CH₃CH₂CHC*l*COO⁻ than in CH₂C*l*CH₂CH₂CH₂COO⁻, dispersing the negative charge on CH₃CH₂CHC*l*COO⁻ to a greater extent, causing CH₃CH₂CHC*l*COOH to be a stronger acid.

[]	Exercise:								
! '	Which	of the following	g se	quences ranks	the	compounds in	increas	sing order of pK _a ?	
	A	C ₆ H₅OH	<	C₂H₅OH	<	CCl₃CO₂H	<	CH₃CO₂H	
	В	C ₆ H ₅ OH	<	C₂H₅OH	<	CH₃CO₂H	<	CCl ₃ CO ₂ H	
	c)	CCl ₃ CO ₂ H	<	CH₃CO₂H	<	C ₆ H₅OH	<	C₂H₅OH	1
	D	CCl ₃ CO ₂ H	<	CH₃CO₂H	<	C₂H₅OH	<	C ₆ H₅OH	-
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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 NH₃ to form salts.

Reaction With	Alcohols, ROH	Phenol, C ₆ H ₅ OH	Carboxylic acid, RCOOH
Na(s)	Redox reaction with effervescence of hydrogen: ROH + Na → RO-Na ⁺ + ½H 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) > RCOO-Na ⁺ + ½H ₂
NaOH(aq)	No reaction. Alcohol is not acidic enough to react with	Acid-base reaction and phenol dissolves: $C_6H_5OH + NaOH$ $\rightarrow C_6H_5O^-Na^+ + H_2O$	Acid-base reaction: RCOOH + NaOH → RCOO⁻Na⁺ + H₂O
Na ₂ CO ₃ (aq)	the reagent.	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, C₅H₅OH	Carboxylic acid, RCOOH	
NaHCO3(aq) NH3(aq)	No reaction. Alcohol is not acidic	No reaction. Phenol is not acidic enough	Acid-base reaction with evolution of CO ₂ : RCOOH + NaHCO ₃ \rightarrow RCOO ⁻ Na ⁺ + H ₂ O + CO ₂	
	enough to react with the reagent.	to react with the reagent.	Acid-base reaction: RCOOH + NH₃ → RCOO⁻NH₄⁺	



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.



- > The reaction is reversible (equilibrium constant is not very large, about 3.4)
- > The equilibrium position is driven to the right by using
 - o an excess of one of the reactants,
 - o 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:

CH₃COOH + HOCH₂CH₃
$$\xrightarrow{\text{catalytic}}_{\text{heat under reflux}}$$
 CH₃COOCH₂CH₂CH₃ + H₂O

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

A carboxylic acid is converted into an acyl chloride ($R < C_{C_1}$) using PCl₃, PCl₅ or SOCl₂.

Reagents / conditions: PC/3, PC/5 or SOC/2

	RCOOH to RCOC/	ROH to RC/		
PC/3	3RCOOH + PC/ ₃ → 3RCOCl + H ₃ PO ₃	3ROH + PC/₃ → 3RCl + H₃PO₃		
DC/	$RCOOH + PCl_5 \to RCOCl + POCl_3 + HCl$	$ROH + PCl_5 \to RCl + POCl_3 + HCl$		
F015	Observation: White fumes of HCI observed.			
5001	$RCOOH + SOCl_2 \rightarrow RCOCl + SO_2 + HCl$	$ROH + SOCl_2 \to RCl + SO_2 + HCl$		
50012	Observation: White fume	s of HC/ 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 SOCl₂ is convenient as the two other products are both gaseous and are easily removed from the reaction mixture.
- HCl 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, LiA/H_4 in dry ether. This **cannot be achieved** using sodium borohydride (NaBH₄), or by heating with H₂ and Ni.

Reagents / conditions : LIAIH₄ in dry ether RCOOH + 4[H] $\xrightarrow{\text{LiA/H_4 in dry ether}}$ RCH₂OH + H₂O

1.5.6 Distinguishing test for carboxylic acids

Test:

Add Na₂CO₃(aq) (or NaHCO₃(aq)) at room temperature.

Observation: Effervescence of CO₂ 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, $\mathbf{r}_{\mathbf{r}}$.

	General structure	Examples	Nomenclature
Carboxylic acid	R-C OH	$CH_3 = C_{OH}^{O}$ $CH_3 = C_{OH}^{O}$ $CH_3 = C_{OH}^{O}$ C_{OH}^{O} C_{OH}^{O} C_{OH}^{O} C_{OH}^{O}	-
Acyl chloride (under the family of acyl halides)	R-C/ C/	CH ₃ -C ⁰ c/ ethanoyl chloride benzoyl chloride	change –ic acid to –yl chloride
Ester	R-C	CH ₃ -C OCH ₂ CH ₃ ethyl ethanoate OCH ₂ CH ₃ ethyl benzoate	change –ic acid to –ate. Name is preceded by alcohol.
Amide	0 R-C ^{//} N-R" R' [/]	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*I* 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



2.3.1.1 Hydrolysis of acyl chlorides



- 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 HCl are evolved.
- Since HCl is very soluble in water, some remain dissolved in solution such that when RCOCl is reacted with water, the resultant solution is strongly acidic (pH ~ 1, due to complete ionisation of HCl).

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:

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

	о R_С_С/	RCH₂C/	⟨◯)—cı
C=O carbon is bonded to 2 highly electronegative atoms, O and C/. factor ⇒ higher δ+ charge on C ⇒ more susceptible to attack by nucleophiles.		C–C/ carbon is bonded to only 1 highly electronegative atom, C/. ⇒ lower δ+ charge on C ⇒ less susceptible to attack by nucleophiles (as compared to RCOC/).	Overlapping of p-orbital on C <i>l</i> atom with π-electron cloud of the benzene ring ⇒ C-C <i>l</i> bond has partial double bond character ⇒ no cleavage occurs due to strengthening of the C-C <i>l</i> bond Electron-rich benzene ring repels nucleophile
Steric factor	 sp² hybridised C=O carbon ⇒ less steric hindrance since nucleophile attacks trigonal planar C 	² hybridised C=O carbon less steric hindrance since nucleophile attacks trigonal planar C sp ³ hybridised C–C <i>l</i> carbon ⇒ more steric hindrance since nucleophile attacks tetrahedral C	
Ease of hydrolysis		RCOCI > RCH ₂ -CI > P	h–C/
Evidence: Reaction with aq. AgNO ₃	White ppt of AgC/ is observed immediately.	No ppt. However, white ppt of AgC/ 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 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° and 2°) to give amides.



Note: Tertiary amines do not react with acyl chlorides.

2.3.2 Reactions of esters

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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 <u>heating under reflux with acid or alkali</u>.

(I) Acidic hydrolysis

$$R^{O} = \frac{HCl(aq)}{Hc} + H_2O = \frac{HCl(aq)}{heat under reflux} R^{O} + R'OH$$

In the acidic hydrolysis of ester, the nucleophile is H₂O.

(II) Alkaline/Basic hydrolysis



In the alkaline hydrolysis of ester, the nucleophile is OH⁻ (stronger nucleophile than H₂O). 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).











RAFFLES INSTITUTION YEAR 6 H2 CHEMISTRY 2023 Tutorial 18 – Carboxylic Acids and Derivatives

Self-check Questions

- 1 Complete the following reaction schemes by drawing the structural formulae of compounds in the boxes and filling in the reagents and conditions where required.
 - A. Preparations and Reactions of Carboxylic Acids



B. Reactions of Acyl Chlorides



- 2 Draw the structural formula for each of the following compounds.
 - (a) methylpropanoic acid
 (b) 3-chloro-2,4-dimethylpentanoic acid
 (c) methyl propanoate
 (d) heptanedioic acid
- 3 Give the IUPAC names for the following compounds:



- 4 Explain the following statements.
 - (a) Hydroxyethanoic acid exists as a solid whereas ethanoic acid exists as a liquid.
 - (b) Ethanoic acid has a higher boiling point of 118 °C but ethyl ethanoate has a boiling point of 77 °C.
 - (c) Benzoic acid is less soluble in water than sodium benzoate.
- 5 Yanucamide B can be extracted from a marine sponge.

Which combination of the number of chiral centres and of ester linkages does it possess?

	number of chiral centres	number of ester linkages
Α	4	2
в	4	3
С	5	2
D	5	3



6 The ester X, which is used in perfumes, has the molecular formula C₆H₁₂O₂. It is found that one of the products of acid hydrolysis of compound X gives a yellow precipitate with alkaline aqueous iodine.

What is the structural formula of compound X?

Δ	CH ₃ CO ₂ CH ₂ CH(CH ₃) ₂	в	CH ₃ CH ₂ CO ₂ CH ₂ CH ₂ CH ₃
c	(CH ₃) ₂ CHCO ₂ CH ₂ CH ₃	D	CH ₃ CH ₂ CH(CH ₃)CO ₂ CH ₃

7 One gram of each of the following compounds was heated with NaOH(aq), followed by the addition of dilute HNO₃(aq) and AgNO₃(aq).

Α	В	С	D
CH3COC/	CH2CI CH2CI	CI CI	
C ₂ H ₃ OC/	C6H10Cl2	C ₆ H ₄ Cl ₂	C4H4O2Cl2
$M_r = 78.5$	M _r = 153	M _r = 147	M _r = 155

Which compound will produce the largest mass of AgC/(s)?

8 The diagram shows the structure of a molecule of the sex hormone oestrone.



Which statements regarding oestrone are correct?

- 1 It gives an orange precipitate with 2,4-dinitrophenylhydrazine.
- 2 It gives hydrogen with metallic sodium.
- 3 It forms an ester with ethanoyl chloride.

Practice Questions

- 1 Rank the following compounds in order of decreasing acid strength and briefly explain your reasoning.
 - (a) phenol, ethanoic acid, ethanol
 - (b) ethanoic acid, trichloroethanoic acid, chloroethanoic acid, trifluoroethanoic acid
- 2 Rank the following compounds in order of decreasing ease of hydrolysis and explain your reasoning.

C_6H_5Cl $C_6H_5CH_2Cl$ C_6H_5COCl

3 Suggest a simple chemical test to distinguish between each pair of compounds.

(a)	C₅H₅COOH	and	C₅H₅OH
(b)	CH ₃ CH ₂ COCI	and	C/CH ₂ CH ₂ COOH
(c)	CH ₃ COOCH ₂ CH ₂ CH ₃	and	CH ₃ COOCH(CH ₃) ₂
(d)	НСООН	and	CH₃COOH

4 Draw the structure of all formula of all products formed when compound A is reacted with the following reagents and conditions respectively.



- (a) H₂SO₄(aq) and heat
- (b) NaOH(aq) and heat
- (c) KMnO₄(aq), H₂SO₄(aq) and heat
- 5 State the reagents and conditions needed for each step and draw the structural formula of the intermediates A to E.



- 6 Compound F, C₈H₈O₂ is insoluble in water but dissolves in NaOH(aq). It reacts with 2,4dinitrophenylhydrazine but not with Fehling's solution. With bromine water, F gives G, C₈H₅O₂Br₃. With alkaline aqueous iodine followed by acidification, F, gives H, C₇H₆O₃. Compound H dissolves in both NaOH(aq) and Na₂CO₃(aq).
 - (a) Deduce the structures of compounds F, G and H. Explain the chemistry of the reactions described.
 - (b) Write a balanced equation for the following reactions.
 - (i) F with 2,4-dinitrophenylhydrazine
 - (ii) F with alkaline aqueous I₂
 - (iii) J with NaOH
 - (iv) H with Na₂CO₃

[N2012/III/5 (modified)]

Malic acid occurs in green apples and grapes. It is often added to beverages and confectionery to confer a sour taste.



(a) Suggest the reagents and conditions you would use in a three-step synthesis of malic acid from bromoethanal, identifying the intermediates G and H.

$$Br \xrightarrow{O} \xrightarrow{\text{step 1}} G \xrightarrow{\text{step 2}} H \xrightarrow{\text{step 3}} \text{malic acid}$$
[5]

- (b) Malic acid can be dehydrated to give a mixture of two isomeric alkenedioic acids with the molecular formula $C_4H_4O_4$.
 - (i) Draw the structures of the isomers and state the type of isomerism they show.
 - (ii) Suggest reagents and conditions for the dehydration reaction.
 - (iii) The pK_a values of the two acidic groups in one isomer, J, are 3.0 and 4.4, whereas in the other isomer, K, they are 1.9 and 6.2.

Use the pK_a values to suggest which isomer, **J** or **K** produces the more stable mono-anion on treatment with 1 mol of NaOH? Explain your answer.

(iv) Draw the displayed formula of the mono-anion produced in (iii) and use your formula to suggest an explanation for why it is more stable than the mono-anion of the other isomer.

Gently heating the anhydrous crystals of one of the isomers **J** or **K** produces a neutral compound L, $C_4H_2O_3$, which does not react with sodium metal or give a precipitate with 2,4-dinitrophenylhydrazine.

Suggest a structure for compound L, and identify which isomer, J or K produces L.
 Explain your answer and write an equation for the reaction. [4]

When malic acid is heated with acidified $K_2Cr_2O_7$, compound N is formed. Heating N in an inert solvent for several hours produces P, $C_3H_4O_3$ and a gas Q. Both N and P react with 2,4-dinitrophenylhydrazine. Compound P also gives a yellow precipitate with aqueous alkaline iodine.

(d) Deduce structures for N and P, and use the information given to suggest the identity of gas Q. [5]

[Total: 20]