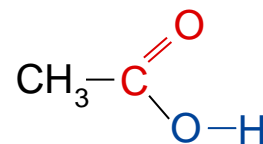


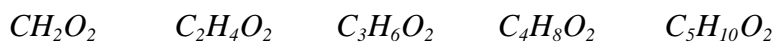
CARBOXYLIC ACIDS

Structure

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



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



Nomenclature

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

e.g. CH₃COOH is called ethanoic acid as it is derived from ethane.

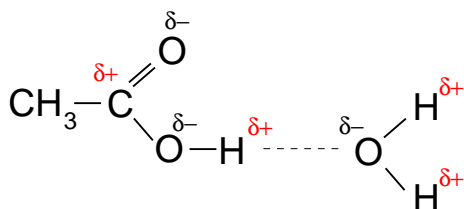
Many carboxylic acids are still known under their trivial names, some having been called after characteristic properties or origin.

Formula	name	(trivial name)	origin of name
HCOOH	methanoic acid	<i>formic acid</i>	latin for ant
CH ₃ COOH	ethanoic acid	<i>acetic acid</i>	latin for vinegar
C ₆ H ₅ COOH	benzenecarboxylic acid	<i>benzoic acid</i>	from benzene

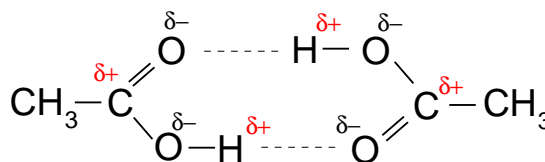
Physical properties

Solubility

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



Intermolecular hydrogen bonding between ethanoic acid and water



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

Boiling point

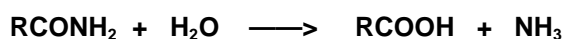
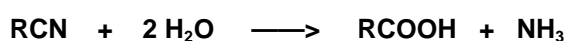
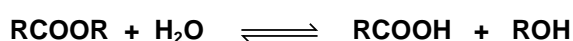
- **increases as size increases** - increased van der Waals forces
- carboxylic acids have high boiling points for their relative mass
- arises from inter-molecular **hydrogen bonding** due to the **polar O—H bonds**
- additional inter-molecular attractions = more energy needed to separate the molecules

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

Compound	Formula	M_r	b. pt. ($^{\circ}\text{C}$)	Comments
ethanoic acid	CH_3COOH	60		
propan-1-ol	$\text{C}_3\text{H}_7\text{OH}$	60		
propanal	$\text{C}_2\text{H}_5\text{CHO}$	58		
butane	C_4H_{10}	58		

Preparation

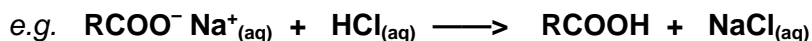
- Oxidation of aldehydes
- Hydrolysis of esters
- Hydrolysis of acyl chlorides
- Hydrolysis of nitriles
- Hydrolysis of amides



CHEMICAL PROPERTIES

- Acidity**
- weak monobasic acids $\text{RCOOH} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{RCOO}^-_{(aq)} + \text{H}_3\text{O}^+_{(aq)}$
 - form salts with alkalis $\text{RCOOH} + \text{NaOH}_{(aq)} \longrightarrow \text{RCOO}^- \text{Na}^+_{(aq)} + \text{H}_2\text{O}_{(l)}$

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



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

Carboxylic acids are strong enough acids to liberate CO_2 from carbonates.

Phenols are also acidic but not are not strong enough to liberate CO_2

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

Reagent(s) Alcohol + acid catalyst (e.g. conc. H_2SO_4)

Conditions Reflux



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

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

propyl ethanoate

ethyl propanoate

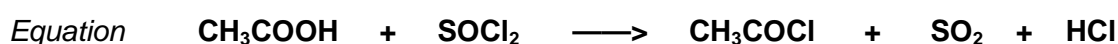
$\text{C}_5\text{H}_{11}\text{COOCH}_3$

HCOOC_2H_5

Chlorination Involves replacing the OH with a Cl to form an acyl chloride

Reagent(s) **thionyl chloride SOCl_2**

Conditions dry conditions

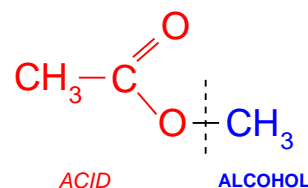


ESTERS - RCOOR'

Structure Substitute an organic group for the H in acids

Nomenclature first part from alcohol, second part from acid

e.g. *methyl ethanoate* $\text{CH}_3\text{COOCH}_3$



Q.3 Draw structures for, and name, all esters of formula $\text{C}_4\text{H}_8\text{O}_2$ and $\text{C}_5\text{H}_{10}\text{O}_2$.
From which acid and alcohol are each derived?

Preparation From **carboxylic acids** or **acyl chlorides**

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

Hydrolysis $\text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{CH}_3\text{OH}$ reflux in **acidic** soln.

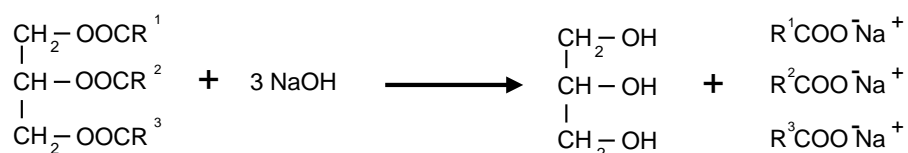
$\text{CH}_3\text{COOCH}_3 + \text{NaOH} \longrightarrow \text{CH}_3\text{COO}^- \text{Na}^+ + \text{CH}_3\text{OH}$ reflux in **alkaline** soln.

Triglycerides

- are the most common component of edible fats and oils.
- are esters of the alcohol glycerol, (propane-1,2,3-triol).

Saponification

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



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

- solvents e.g.
- plasticisers e.g.
- "fruity" food flavouring e.g.

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

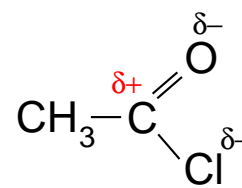
DERIVATIVES OF CARBOXYLIC ACIDS

ACYL (ACID) CHLORIDES - RCOCl

Nomenclature

Named from corresponding acid
 - remove *-ic* add *-yl chloride*

CH_3COCl ethanoyl (*acetyl*) chloride
 $\text{C}_6\text{H}_5\text{COCl}$ benzene carbonyl (*benzoyl*) chloride



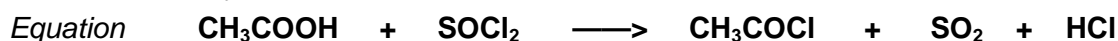
*polarity of bonds
in acyl chlorides*

Preparation Involves replacing the OH of a carboxylic acid with a Cl atom

Method 1

Reagent(s) **thionyl chloride SOCl_2**

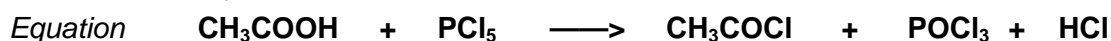
Conditions dry conditions



Method 2

Reagent(s) **phosphorus(V) chloride PCl_5**

Conditions dry conditions



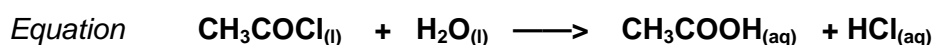
Chemical Properties

- colourless liquids which fume in moist air
- attacked at the positive carbon centre by nucleophiles
- nucleophiles include water, alcohols, ammonia and amines
- undergo addition-elimination reactions
- MUCH MORE REACTIVE THAN CARBOXYLIC ACIDS AND ACID ANHYDRIDES

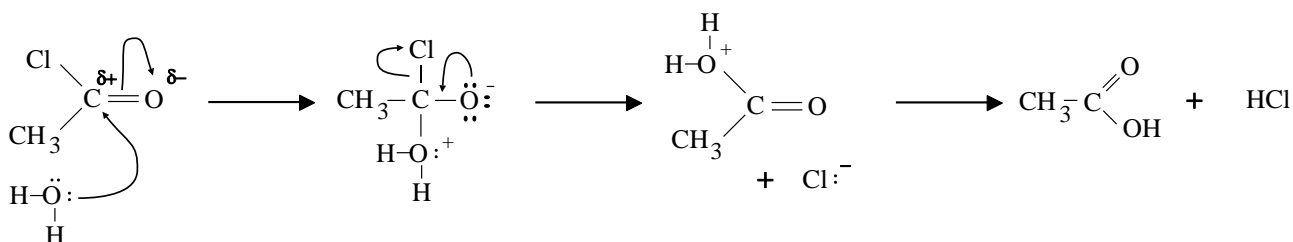
Water

Product(s) carboxylic acid + HCl (fume in moist air / strong acidic solution formed)

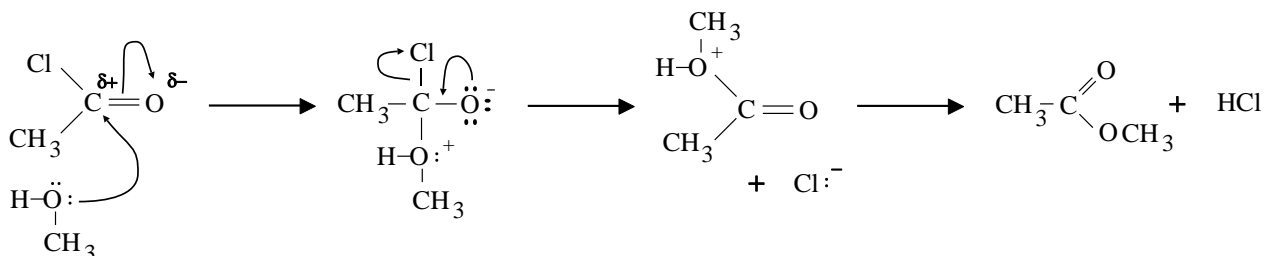
Conditions cold water



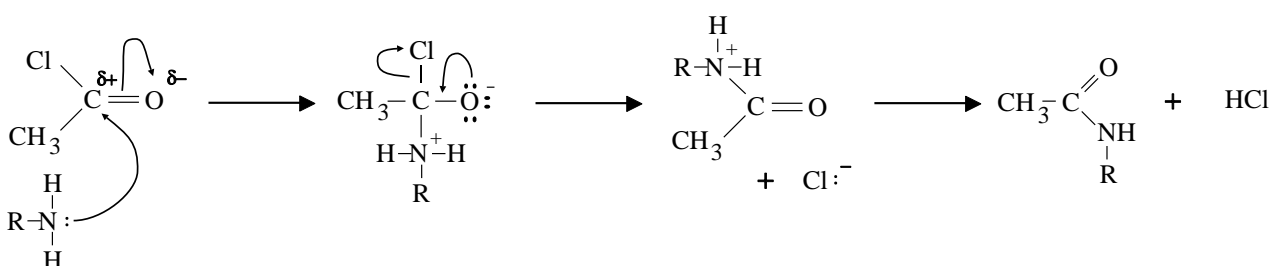
Mechanism addition-elimination



Alcohols	<i>Product(s)</i>	ester + hydrogen chloride
	<i>Conditions</i>	reflux in dry (anhydrous) conditions
	<i>Equation</i>	$\text{CH}_3\text{COCl}_{(l)} + \text{CH}_3\text{OH}_{(l)} \longrightarrow \text{CH}_3\text{COOCH}_3_{(l)} + \text{HCl}_{(g)}$
	<i>Mechanism</i>	addition-elimination



Amines	<i>Product(s)</i>	N-substituted amide + hydrogen chloride
	<i>Conditions</i>	anhydrous
	<i>Equation</i>	$\text{CH}_3\text{COCl}_{(l)} + \text{C}_2\text{H}_5\text{NH}_2_{(aq)} \longrightarrow \text{CH}_3\text{CONHC}_2\text{H}_5_{(s)} + \text{HCl}_{(g)}$ or $\text{CH}_3\text{COCl}_{(l)} + 2\text{C}_2\text{H}_5\text{NH}_2_{(aq)} \longrightarrow \text{CH}_3\text{CONHC}_2\text{H}_5_{(s)} + \text{C}_2\text{H}_5\text{NH}_3\text{Cl}_{(s)}$
	<i>Mechanism</i>	addition-elimination



Ammonia	<i>Product(s)</i>	Amide + hydrogen chloride
	<i>Conditions</i>	Low temperature and excess ammonia. Vigorous reaction.
	<i>Equation</i>	$\text{CH}_3\text{COCl}_{(l)} + \text{NH}_3_{(aq)} \longrightarrow \text{CH}_3\text{CONH}_2_{(s)} + \text{HCl}_{(g)}$ or $\text{CH}_3\text{COCl}_{(l)} + 2\text{NH}_3_{(aq)} \longrightarrow \text{CH}_3\text{CONH}_2_{(s)} + \text{NH}_4\text{Cl}_{(s)}$
	<i>Mechanism</i>	addition-elimination

Q.5 State the reagents used to synthesise...

