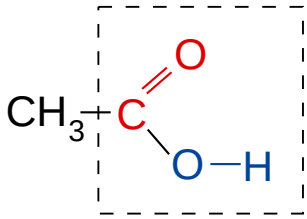
CARBOXYLIC ACIDS

Structure

- contain the carboxyl functional group COOH
- includes a **carb**onyl (**C=O**) group *and* a hydr**oxyl** (**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 :-*

CH_2O_2 $C_2H_4O_2$ $C_3H_6O_2$ $C_4H_8O_2$ $C_5H_{10}O_2$

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

e.g. CH_3COOH *is called ethanoic acid as it is derived from ethane*.

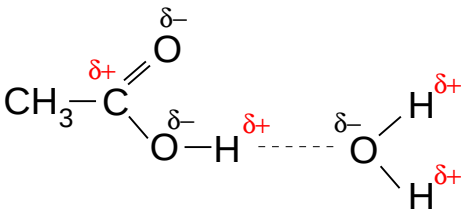
Many carboxylic acids are still known under their trivial names, some having been called after characteristic properties or origin.

Formula	name	(trivial name)	origin of name
HCOOH	methanoic acid	*formic acid*	latin for ant
CH_3COOH	ethanoic acid	*acetic acid*	latin for vinegar
C_6H_5COOH	benzenecarboxylic acid	*benzoic acid*	from benzene

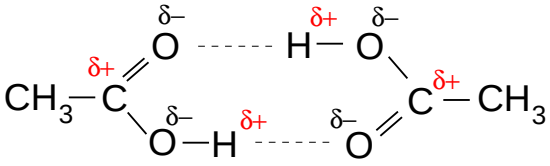
Physical properties

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 induced dipole-dipole interactions
- 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 to separate the molecules

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

Compound	Formula	M_r	b. pt. (°C)	Comments
butane	C_4H_{10}	58	-0.5	***induced dipole-dipole interaction***
propanal	C_2H_5CHO	58	49	**+** ***permanent dipole-dipole***
propan-1-ol	C_3H_7OH	60	97	**+** ***hydrogen bonding***
ethanoic acid	**CH_3COOH**	**60**	**118**	**+** ***hydrogen bonding***

Preparation

- *Oxidation of aldehydes* — **RCHO + [O] —> RCOOH**
- *Hydrolysis of esters* — **RCOOR + H_2O ⇌ RCOOH + ROH**
- *Hydrolysis of acyl chlorides* — **RCOCl + H_2O —> RCOOH + HCl**
- *Hydrolysis of nitriles* — **RCN + 2 H_2O —> RCOOH + NH_3**
- *Hydrolysis of amides* — **$RCONH_2$ + H_2O —> RCOOH + NH_3**

CHEMICAL PROPERTIES

Acidity • weak monobasic acids **RCOOH + H_2O**(l) $\rightleftharpoons$ **$RCOO^-$**(aq) + **H_3O^+**(aq)

They act as typical acids in the following reactions with...

Carbonates
- Produce a **salt** and **carbon dioxide**
- **2 RCOOH + Na_2CO_3**(s) **—> 2 $RCOO^-Na^+$**(aq) **+ CO_2**(g) **+ H_2O**(l)

ANALYTICAL USE

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

Alkalis
- form salts with alkalis **RCOOH + NaOH**(aq) **—> $RCOO^-Na^+$**(aq) **+ H_2O**(l)
  soluble
- the acid can be liberated from its salt by treatment with a stronger acid.

e.g. **$RCOO^-Na^+$**(aq) **+ HC*l***(aq) **—> RCOOH + NaC*l***(aq)

Practical use *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.*

Metals
- Products: a **salt** and **hydrogen**

2RCOOH + Mg(s) **—> $(RCOO^-)_2Mg^{2+}$**(aq) **+ H_2**(g)

Metal oxides
- Products: a **salt** and **water**

2RCOOH + MgO(s) **—> $(RCOO^-)_2Mg^{2+}$**(aq) **+ H_2O**(l)

Chlorination

Reagent(s)	**thionyl chloride $SOCl_2$**
Conditions	dry conditions
Product	**acyl chloride**
Equation	**CH_3COOH + $SOCl_2$ —> CH_3COCl + SO_2 + HC*l***
Use	*Acyl chlorides are reactive and useful in synthesis*

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

Reagent(s) Alcohol + acid catalyst (eg conc. H_2SO_4)

Conditions Reflux

Equation $CH_3COOH + CH_3OH \rightleftharpoons CH_3COOCH_3 + H_2O$

ethanoic acid ***methanol*** ***methyl ethanoate***

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

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

propyl ethanoate

ethyl propanoate

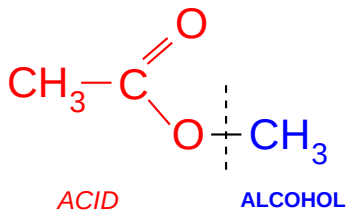
$HCOOC_2H_5$

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*** *CH_3COOCH_3*



Q.3 *Draw structures for, and name, all esters of formula $C_4H_8O_2$ and $C_5H_{10}O_2$. From which acid and alcohol are each derived?*

Synthesis From carboxylic acids — slow, equilibrium process
acyl chlorides — faster, but more care must be taken

Properties
- colourless liquids which are insoluble in water
- unreactive

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

Hydrolysis $CH_3COOCH_3 + H_2O \rightleftharpoons CH_3COOH + CH_3OH$ reflux in **acid** soln.

$CH_3COOCH_3 + NaOH \longrightarrow CH_3COO^-Na^+ + CH_3OH$ reflux in **alkali**

very soluble in water

In the presence of alkali, the carboxylic acid reacts to form a soluble sodium salt; addition of dilute hydrochloric acid will liberate the carboxylic acid

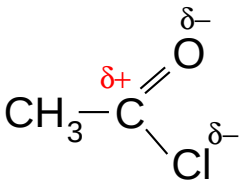
USES Despite being fairly chemically unreactive substances, **esters are useful** as ...

- solvents *eg*
- plasticisers *eg*
- "fruity" food flavouring *eg*

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

DERIVATIVES OF CARBOXYLIC ACIDS

ACYL (ACID) CHLORIDES - RCOC*l*



polarity of bonds in acyl chlorides

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

CH_3COCl ethanoyl *(acetyl)* chloride
C_6H_5COCl benzene carbonyl *(benzoyl)* chloride

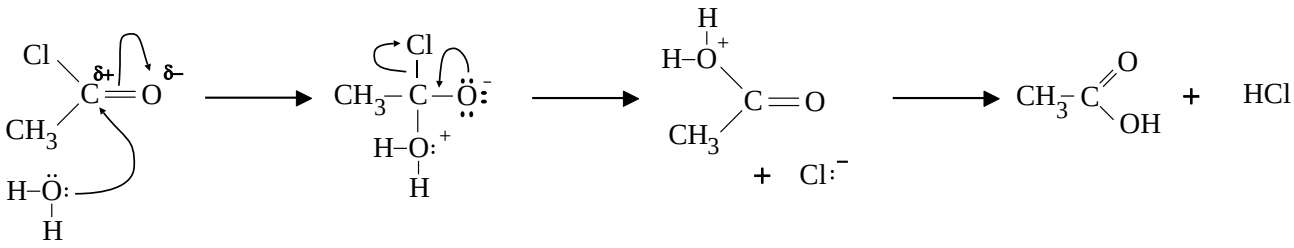
Preparation Involves replacing the OH of a carboxylic acid with a C*l* atom

Method 1
Reagent(s) **thionyl chloride $SOCl_2$**
Conditions dry conditions
Equation **CH_3COOH + $SOCl_2$ —> CH_3COCl + SO_2 + HC*l***

Method 2
Reagent(s) **phosphorus(V) chloride PCl_5**
Conditions dry conditions
Equation **CH_3COOH + PCl_5 —> CH_3COCl + $POCl_3$ + HC*l***

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 + HC*l* (fume in moist air / strong acidic solution formed)
Conditions cold water
Equation **CH_3COCl**(l) + **H_2O**(l) —> **CH_3COOH**(aq) + **HC*l***(aq)
Mechanism addition-elimination

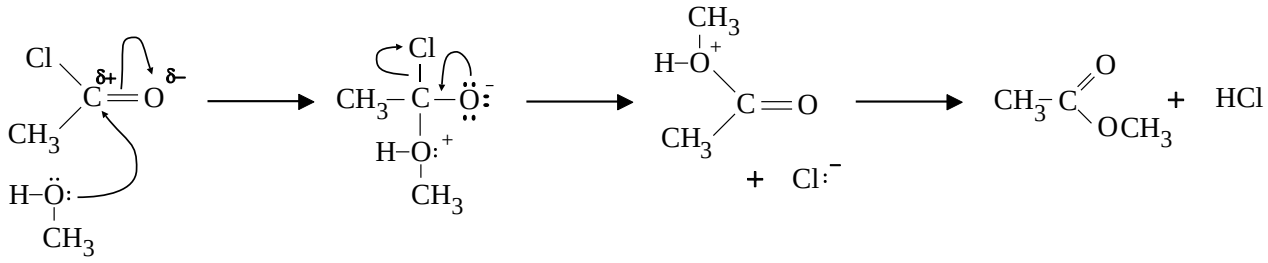


Alcohols *Product(s)* ester + hydrogen chloride

Conditions reflux in dry (anhydrous) conditions

Equation **CH_3COCl**(l) **+** **CH_3OH**(l) **—>** **CH_3COOCH_3**(l) **+** **HCl**(g)

Mechanism addition-elimination



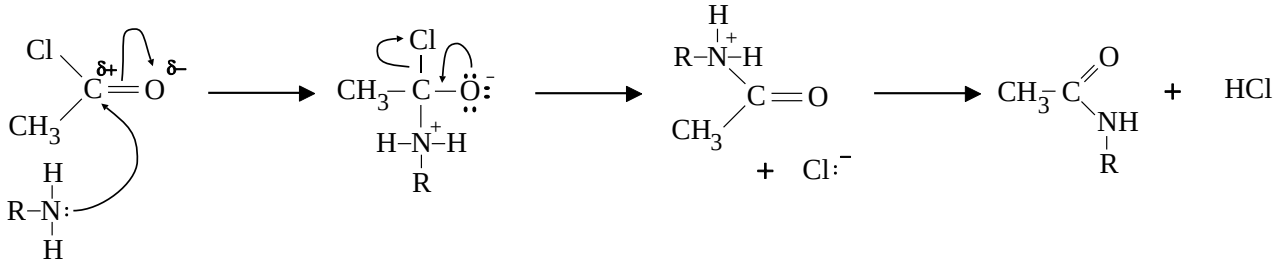
Amines *Product(s)* N-substituted amide + hydrogen chloride

Conditions anhydrous

Equation **CH_3COCl**(l) **+** **$C_2H_5NH_2$**(aq) **—>** **$CH_3CONHC_2H_5$**(s) **+** **HCl**(g)

or **CH_3COCl**(l) **+** **$2C_2H_5NH_2$**(aq) **—>** **$CH_3CONHC_2H_5$**(l) **+** **$C_2H_5NH_3Cl$**(s)

Mechanism addition-elimination



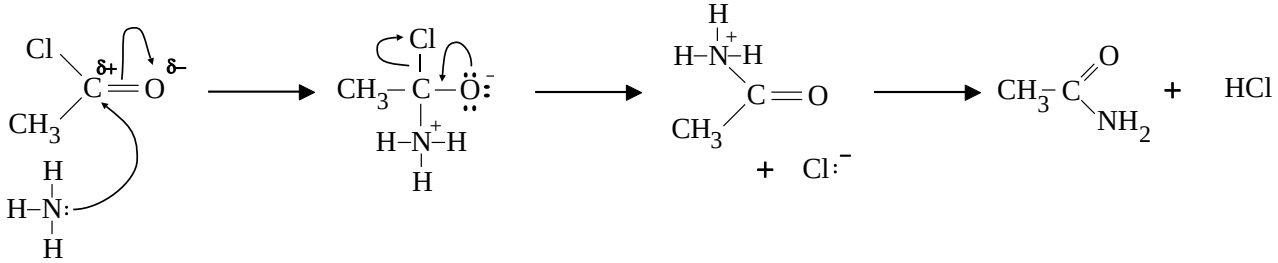
Ammonia *Product(s)* Amide + hydrogen chloride

Conditions Low temperature and excess ammonia. Vigorous reaction.

Equation **CH_3COCl**(l) **+** **NH_3**(aq) **—>** **CH_3CONH_2**(s) **+** **HCl**(g)

or **CH_3COCl**(l) **+** **$2NH_3$**(aq) **—>** **CH_3CONH_2**(s) **+** **NH_4Cl**(s)

Mechanism addition-elimination



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

$C_6H_5CON(CH_3)_2$

$C_3H_7COOCH_3$

C_2H_5COOH