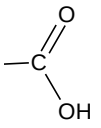
CARBOXYLIC ACIDS

= derivatives of hydrocarbons containing at least one ..... group



..... group

..... group

Naming

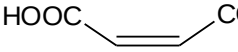
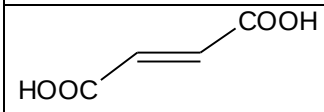
Saturated monocarboxylic acids

HCOOH	methanoic acid	formic acid	mravenčí kyselina
	ethanoic acid	acetic acid	
	propanoic acid	propionic acid	
$CH_3CH_2CH_2COOH$		butyric acid	
$CH_3(CH_2)_3COOH$		valeric acid	
$CH_3(CH_2)_4COOH$		caproic acid	
	hexadecanoic acid		
	octadecanoic acid		

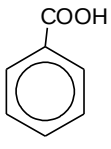
Unsaturated monocarboxylic acids

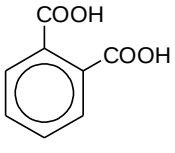
CH_2=CHCOOH		acrylic acid	
	hexa-2,4-dienoic acid	sorbic acid	
$CH_3(CH_2)_7CH$=$CH(CH_2)_7COOH$			

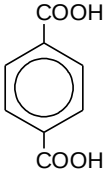
Dicarboxylic acids

HOOC – COOH	ethanedioic acid	oxalic acid	šťavelová kyselina
HOOC – CH_2 – COOH		malonic acid	
HOOC – $(CH_2)_2$ – COOH		succinic acid	jantarová kyselina
	pentanedioic acid		glutarová kyselina
	hexanedioic acid		adipová kyselina
		maleic acid	
		fumaric acid	

Aromatic acids





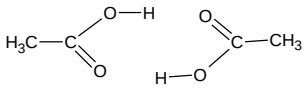


Properties of carboxylic acids

1. *Put the following acids in order with respect to increasing melting point: propanedioic acid (M_r = 104), butanedioic acid (M_r = 118), pentanoic acid (M_r = 102).*

2. *Put the following acids with respect to decreasing solubility in water: C_4H_9COOH, $HOOC(CH_2)_2COOH$, $C_{10}H_{22}COOH$*

Ethanoic acid forms a dimer due to ....



Reactivity of carboxylic acids

1. Weak acids

   R-COOH + H_2O →

   3. *Explain the fact that the strength of carboxylic acids decreases with increasing number of carbon atoms.*

   4. *Put the following acids in order with respect to decreasing acidity: palmitic acid, formic acid, butanoic acid.*

   Like all acids carboxylic acids react with metals, hydroxides, metal oxides, carbonates forming salts:

   5. *Finish equations and name the products:*

   $CH_3COOH + MgO \rightarrow$

   $CH_3COOH + Na \rightarrow$

   $CH_3COOH + CaCO_3 \rightarrow$

   $NaOH + C_6H_5COOH \rightarrow$

   $Mg(OH)_2 + C_{17}H_{34}COOH \rightarrow$

   $Al(OH)_3 + CH_3COOH \rightarrow$

   Sodium and potassium salts of fatty acids are soaps, e.g. sodium palmitate or sodium stearate.

   6. *How does soap work?*

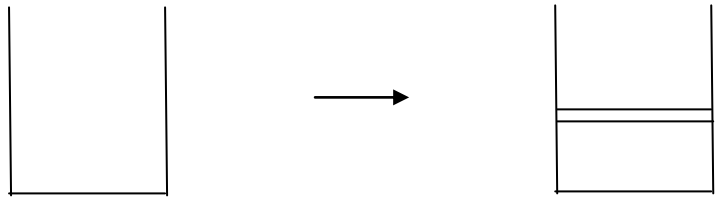
2. Decarboxylation = elimination of carbon dioxide from acids or their salts at high temperatures in the presence of NaOH

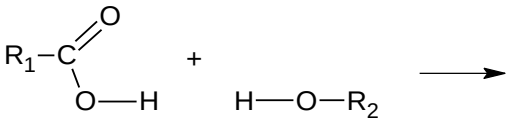
   $R{-}COONa + NaOH \rightarrow R{-}H + Na_2CO_3$

7. *$CH_3COONa + NaOH \rightarrow$*

8. *$C_6H_5COOH + NaOH \rightarrow$*

3. Esterification = condensation reaction between carboxylic acids and alcohols in the presence of an acidic catalyst.
(**Condensation** =





Neutralization:	✖	Esterification:
Acids give		Acids give .....
Hydroxides give		Alcohols give .....

9. *Finish equations and name the esters:*

$HCOOH + C_2H_5OH \rightarrow$

$C_2H_5COOH + CH_3OH \rightarrow$

$HCOOH + C_3H_7OH \rightarrow$

$C_6H_5COOH + C_2H_5OH \rightarrow$

$C_4H_9OH + C_3H_7COOH \rightarrow$

$CH_3OH + C_2H_5COOH \rightarrow$

10. *Write down the equations for esterifications leading to the formation of:*

methyl butanoate

propyl benzoate

butyl ethanoate

ethyl propanoate

Preparation and manufacture of carboxylic acids

- **Aliphatic acids:** oxidation of ..... alcohols or ....., oxidising agents: ....., ..., O_2,…

  ethanoic acid:

  1. hydration of ethyne + oxidation

  $HC{\equiv}CH + H_2O \rightarrow$ ..... $\rightleftarrows$ ..... $\xrightarrow{ox.}$ ..... for industrial purposes

  2. oxidation of ethanol

  $C_2H_5OH + O_2 \rightarrow CH_3COOH + H_2O$

  making vinegar = 8% solution of acetic acid, this process is catalysed by enzymes of vinegar fermentation (bacteria Mycoderma aceti)

- **Aromatic acids:** oxidation of hydrocarbons

Importance and uses of some carboxylic acids

Methanoic (formic) acid

Ethanoic (acetic) acid

Oxalic acid

Terephthalic acid

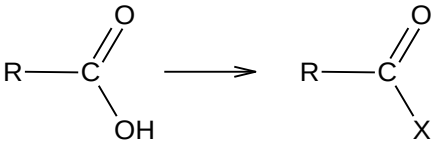
Benzoic acid

Sorbic acid.

DERIVATIVES OF CARBOXYLIC ACIDS

FUNCTIONAL DERIVATIVES

Change in the functional group – OH is substituted by another group.



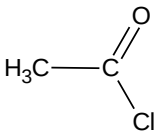
X - halogen ⇒
- OR ⇒
- OCOR` ⇒
- NH_2
- NHR
- NR_2

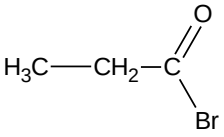
Halides

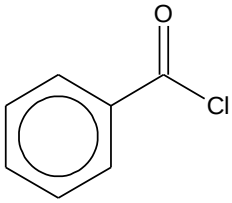
Liquids soluble in some polar solvents, cause burns of skin, irritate eyes, synthetic intermediates

Naming: -oyl halide

11. *Name these halides*



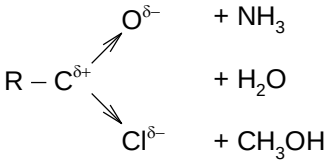




12. *Write the structures for:*

methanoyl bromide ethanoyl (acetyl) iodide butanoyl chloride

Reactions: Not only the oxygen atom but also the halogen atom pulls out electrons from the carbon atom. The positive charge made this way attracts *nucleophiles/electrophiles/free radicals*.



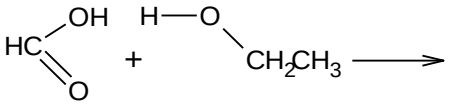
Esters

Esterification: acid + alcohol → ester + water

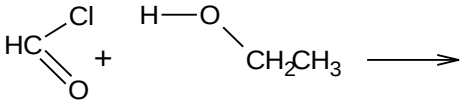
Preparation:

1. Alcohol + acid in the presence of acidic catalyst (H_2SO_4)

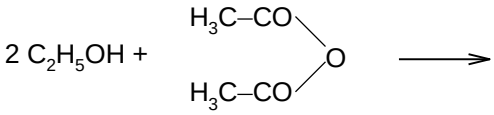
The water molecule is formed by OH group from an acid and hydrogen atom from an alcohol.



2. alcohol + acid halide



3. alcohol + acid anhydride



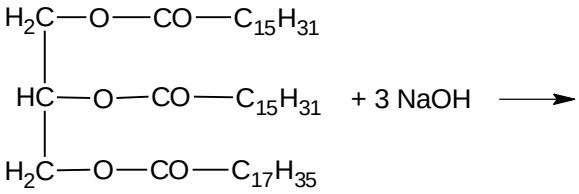
Properties:

Lower esters are liquids, esters of long chain acids are solid, and they are well soluble in polar organic substances, less soluble in water. Esters are less reactive than acids.

Reactions: hydrolysis

- Acidic $HCOOC_2H_5 + H_2O \xrightarrow{H^+}$
- Alkaline $HCOOC_2H_5 + NaOH \rightarrow$

  saponification of fats

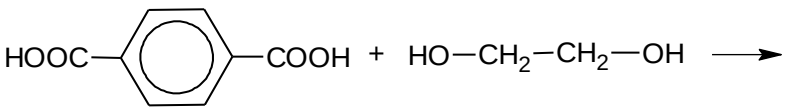


Uses and importance:

natural esters =

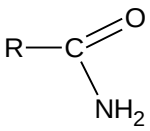
artificial flavorings

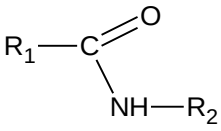
polyesters = synthetic fibers, PET flasks, ...

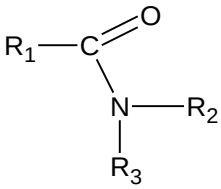


Amides

Three types:







Naturally occurring amides = peptides and proteins, contain peptide link (see aminoacids)

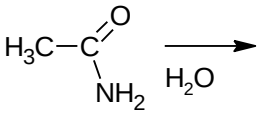
Naming: -amide

$HCONH_2$ methanamide (formamide)

CH_3CONH_2 ethanamide (acetamide)

Properties:

Methanamide is a liquid, other amides are solids. In the presence of strong inorganic acids amides decompose to acids and ammonia.



Preparation: from halides

R-COCl + NH_3 →

Uses: polyamides (PAD) = synthetic fibres, from diamines and dicarboxylic acids

Nylon = nylon6-6

Silon = nylon 6

Anhydrides:

Naming: acid anhydride

Water molecule is removed from:

- two molecules of monocarboxylic acid

13. *Write the structure of an anhydride made from two molecules of ethanoic acid.*

- one molecule of dicarboxylic acid (internal anhydrides)

14. *Write the structure of an anhydride made by dehydration of phthalic (benzene-1,2-dioic) acid.*

Anhydrides are more reactive than esters and amides

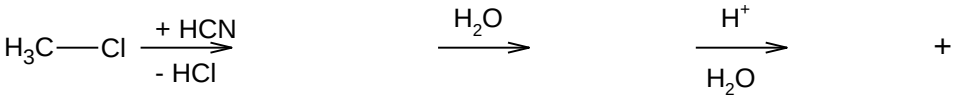
Nitriles

Derivatives of carboxylic acid, nitrogen atom substitutes both –OH and =O group. Nitriles contain −C≡N group.

Naming: ethanenitrile butanenitrile $C_5H_{11}CN$ C_2H_5CN

15. *Suggest why the name methanenitrile is not used.*

Properties and uses: toxic liquids well soluble in polar organic solvents. The most important reaction = hydrolysis, product of hydrolysis are amides or acids. This reaction is used for making carboxylic acid. Nitriles are made by a reaction between a halogenoalkane and HCN.



16. *Suggest one more way to make nitriles.*

Propenonitrile = acrylonitrile ..... is used for making synthetic fibres polyacrylonitrile

17. *Write the equation for the polymerization of propenonitrile*

18. *Find the uses of polyacrylonitrile fibres.*

SUBSTITUTIONAL DERIVATIVES

Derivatives made by substituting at least one hydrogen atom in the carbon chain. Greek letters express the position of the substituent.

5 4 3 2 1 used with systematic names

$CH_3 – CH_2 – CH_2 – CH_2 – COOH$

δ γ β α used with trivial names

Halogenoacids

Naming: similar to the naming of halogenoalkanes

CH_3 –CHCl – COOH 2- chloropropanoic acid, α - chloropropionic acid

Preparation: halogenation of carboxylic acids

Properties, uses: toxic substances well soluble in *polar organic solvents/water*, halogenoacids are *weaker/stronger* acids than not substituted acids.

19. *Put $CHCl_2COOH$, CCl_3COOH, $CH_2ClCOOH$ and CH_3COOH in order with respect to increasing acidity.*

A halogen atom may be easily substituted by other functional groups ⇒ synthesis of other derivatives.

$Cl – CH_2 – COOH + H_2O \rightarrow$

$Cl – CH_2 – COOH + NH_3 \rightarrow$

$Cl – CH_2 – COOH + C_6H_5 – O^- Na^+ \rightarrow$

Hydroxyacids

Naming: prefix **hydroxy-** or trivial names

20. Write the structures of the following acids.

Salicylic acid = o-hydroxybenzoic acid, isolated from the bark of willow tree (salix)

Lactic acid = α- hydroxypropionic acid (..... kyselina)

21. Lactic acid shows optical isomerism. Draw the structures for both enantiomers.

Formed by fermentation of saccharides in ..... (responsible for sour taste of curdled milk), ... or ..... When a body has insufficient oxygen for complete oxidation of glucose to carbon dioxide (..... .....) lactate ion is formed in the muscles by ..... oxidation and it causes .....

Tartaric acid (vinná kyselina) = 2,3-dihydroxybutanedioic acid

Major acid in wine, its potassium salt forms crystals of "wine diamonds".

22. How many chiral centres are there in the molecule of tartaric acid? How many enantiomers of tartaric acid exist?

Citric acid = 2-hydroxy- 1,2,3-propanetricarboxylic acid

Used in food industry as a ..... or for its ..... taste.

Produced industrially from ..... by a fungus aspergillums negri. Citrate ion is an intermediate in a citric cycle = a part of metabolic pathways in a human body converting carbohydrates, fats and proteins to..... and ..... and producing energetically rich molecules such as .....

Acetylsalicylic acid = aspirin (Acylpyrin, Anopyrin, Superpyrin)

analgesics, antipyretics, produced by a reaction between salicylic acid and acetic anhydride.

23. Write the equation for the production of aspirin.

Aminoacids

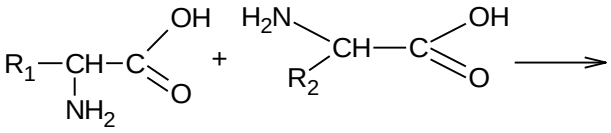
Naming: amino- or trivial names (aminoacids in proteins)

NH_2CH_2COOH 2-aminoethanoic acid = α–aminoacetic acid = glycine

CH_3CHNH_2COOH 2-aminopropanoic acid = α–aminopropionic acid = alanine

Properties: white solids soluble in water, in solid state and in neutral solutions exist as dipolar ions $NH_3^+ CH_2COO^-$ zwitterion (obojetný ion, amfion), result of an internal acid–base reaction

React both with acids and bases. Two molecules of aminoacids join to form dipeptides.



Uses: flavour additives

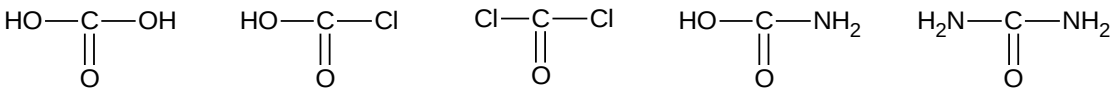
Aspartam (asparagine + phenylalanine dipeptide) … sweet taste

Sodium glutamate = flavour enhancer (intensify the flavour of other food components)

Ketoacids

Contain carbonyl group. The most important is 2- oxopropanoic (**pyruvic**) **acid**, takes part in metabolism in the form of pyruvate ion.

Functional derivatives of carbonic acid



Phosgene: poisonous gas, $CO + Cl_2 \rightarrow COCl_2$, hydrolyses to CO_2 and HCl (reason why it is toxic), reacts with ammonia forming urea

Urea: white crystalline solid, product of metabolism of proteins (aminoacids), decomposes to carbon dioxide and ammonia.

24. *Write the equations for:*
    a. *hydrolysis of phosgene*

    b. *hydrolysis of urea*