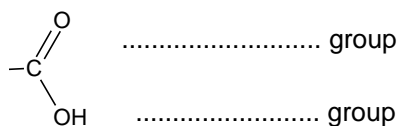


CARBOXYLIC ACIDS

= derivatives of hydrocarbons containing at least one group



Naming

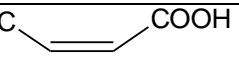
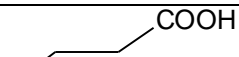
Saturated monocarboxylic acids

HCOOH	methanoic acid	formic acid	mravenčí kyselina
	ethanoic acid	acetic acid	
	propanoic acid	propionic acid	
CH ₃ CH ₂ CH ₂ COOH		butyric acid	
CH ₃ (CH ₂) ₃ COOH		valeric acid	
CH ₃ (CH ₂) ₄ COOH		caproic acid	
	hexadecanoic acid		
	octadecanoic acid		

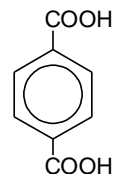
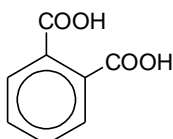
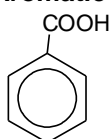
Unsaturated monocarboxylic acids

CH ₂ =CHCOOH		acrylic acid	
	hexa-2,4-dienoic acid	sorbic acid	
CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ COOH			

Dicarboxylic acids

HOOC – COOH	ethanedioic acid	oxalic acid	šŕavelová kyselina
HOOC – CH ₂ – COOH		malonic acid	
HOOC – (CH ₂) ₂ – COOH		succinic acid	jantarová kyselina
	pentanedioic acid		glutarová kyselina
	hexanedioic acid		adipová kyselina
HOOC  COOH		maleic acid	
HOOC  COOH		fumaric acid	

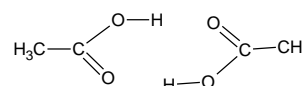
Aromatic acids



Properties of carboxylic acids

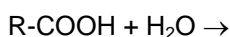
- Put the following acids in order with respect to increasing melting point: propanedioic acid ($M_r = 104$), butanedioic acid ($M_r = 118$), pentanoic acid ($M_r = 102$).
- Put the following acids with respect to decreasing solubility in water: C_4H_9COOH , $HOOC(CH_2)_2COOH$, $C_{10}H_{22}COOH$

Ethanoic acid forms a dimer due to



Reactivity of carboxylic acids

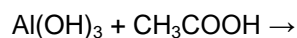
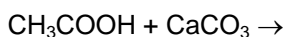
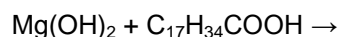
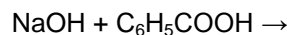
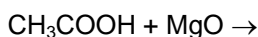
- Weak acids



- Explain the fact that the strength of carboxylic acids decreases with increasing number of carbon atoms.
- 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:

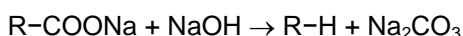
- Finish equations and name the products:



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

- How does soap work?

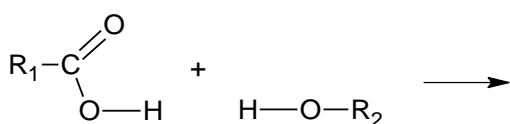
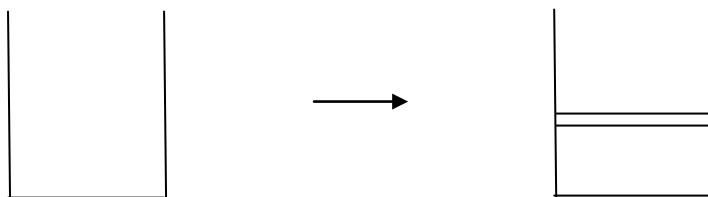
- Decarboxylation = elimination of carbon dioxide from acids or their salts at high temperatures in the presence of NaOH





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

(**Condensation** =



Neutralization:

Acids give

Hydroxides give

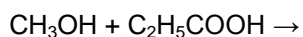
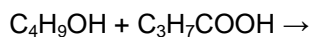
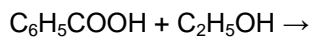
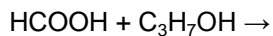
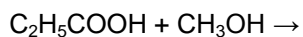
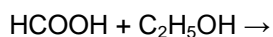
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Esterification:

Acids give

Alcohols give

9. *Finish equations and name the esters:*



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

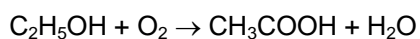
- **Aliphatic acids:** oxidation of alcohols or, oxidising agents:,, O_2, \dots

ethanoic acid:

1. hydration of ethyne + oxidation

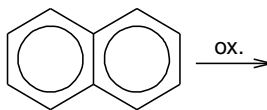
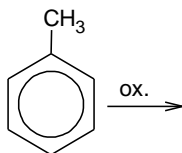
$HC\equiv CH + H_2O \rightarrow \dots \rightleftharpoons \dots \xrightarrow{ox.} \dots$ for industrial purposes

2. oxidation of ethanol



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

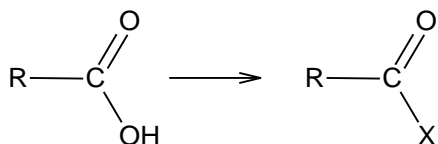
Benzoic acid

Sorbic acid.

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DERIVATIVES OF CARBOXYLIC ACIDS

FUNCTIONAL DERIVATIVES

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



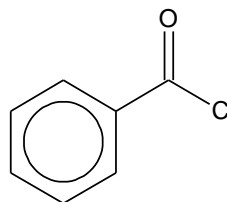
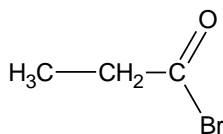
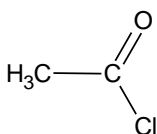
- | | | | |
|---|-------------------------|-------------------|---|
| X | - halogen \Rightarrow | - NH ₂ | } |
| | - OR \Rightarrow | - NHR | |
| | - OCOR' \Rightarrow | - NR ₂ | |

Halides

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

Naming: -oyl halide

11. Name these halides



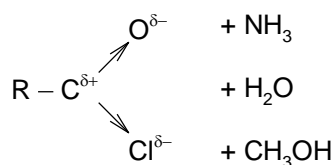
12. Write the structures for:

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

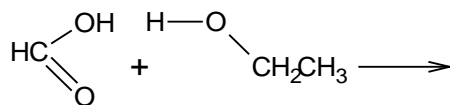
Esterification: acid + alcohol \rightarrow ester + water

Preparation:

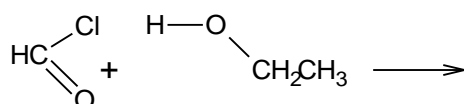
INVESTICE DO ROZVOJE VZDĚLÁVÁNÍ

 1. Alcohol + acid in the presence of acidic catalyst (H₂SO₄)

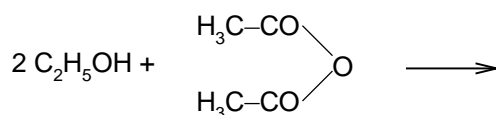
The water molecule is formed by OH group from an acid and hydrogen atom from an alcohol.



2. alcohol + acid halide



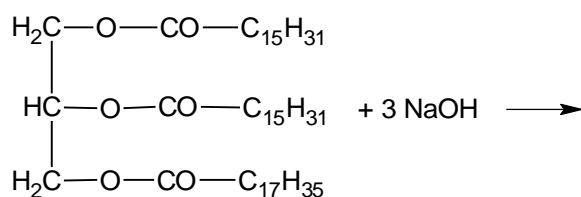
3. alcohol + acid anhydride


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

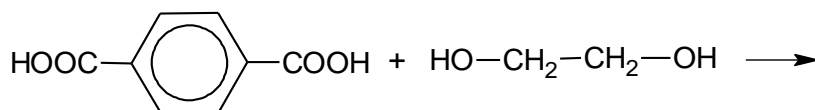
- Acidic $\text{HCOOC}_2\text{H}_5 + \text{H}_2\text{O} \xrightarrow{\text{H}^+}$
- Alkaline $\text{HCOOC}_2\text{H}_5 + \text{NaOH} \rightarrow$
saponification of fats


Uses and importance:

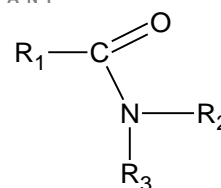
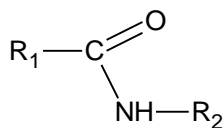
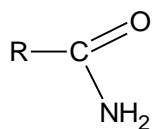
natural esters =

artificial flavorings

polyesters = synthetic fibers, PET flasks, ...


Amides

Three types:



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

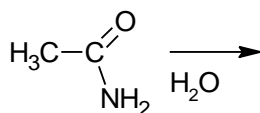
Naming: -amide

HCONH₂ methanamide (formamide)

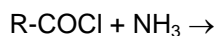
CH₃CONH₂ ethanamide (acetamide)

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



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



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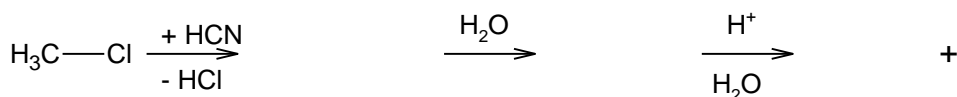
Nitriles

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

Naming: ethanenitrile butanenitrile C₅H₁₁CN C₂H₅CN

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.

Propenenitrile = acrylonitrile is used for making synthetic fibres polyacrylonitrile

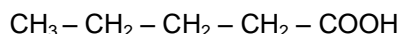
17. Write the equation for the polymerization of propenenitrile

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



δ γ β α used with trivial names

Halogenoacids

Naming: similar to the naming of halogenoalkanes



Preparation: halogenation of carboxylic acids

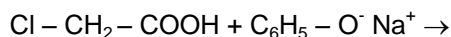
Properties, uses: toxic substances well soluble in *polar organic solvents/water*, halogenoacids are *weaker/stronger* acids than not substituted acids.

19. Put CHCl₂COOH, CCl₃COOH, CH₂ClCOOH and CH₃COOH in order with respect to increasing acidity.



INVESTICE DO ROZVOJE VZDĚLÁVÁNÍ

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



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)

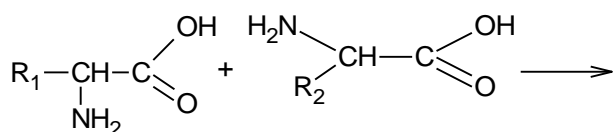
$\text{NH}_2\text{CH}_2\text{COOH}$ 2-aminoethanoic acid = α -aminoacetic acid = glycine

$\text{CH}_3\text{CHNH}_2\text{COOH}$ 2-aminopropanoic acid = α -aminopropionic acid = alanine

Properties: white solids soluble in water, in solid state and in neutral solutions exist as dipolar ions

$\text{NH}_3^+\text{CH}_2\text{COO}^-$ 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

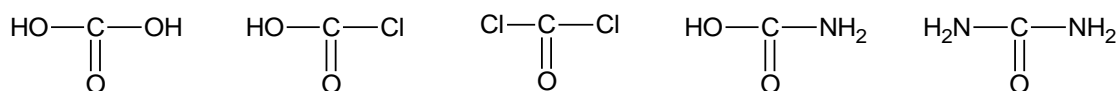
Aspartam (asparagine + phenylalanine dipeptide) ... sweet taste

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, $\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$, 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



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