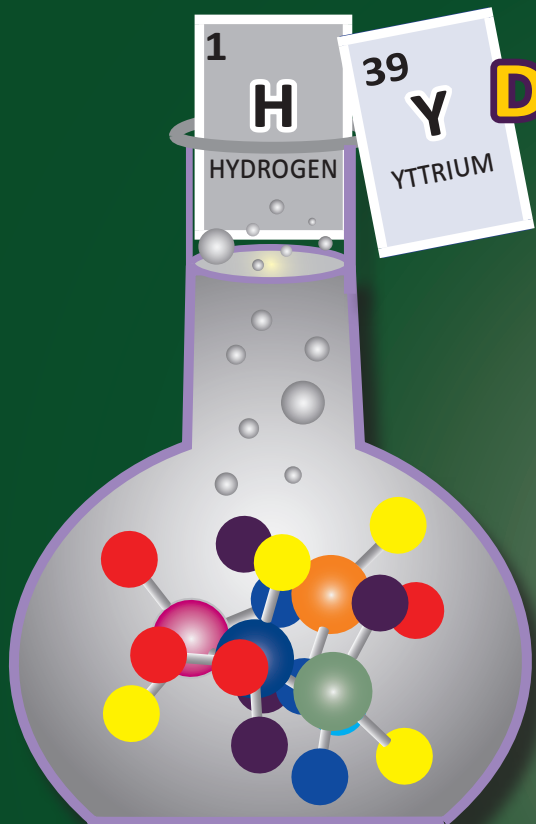




DERIVATIVES

ALCOHOLS
PHENOLS
ALDEHYDES
KETONES
CARBOXYLIC ACIDS
AMINES
AMINO ACIDS



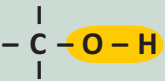
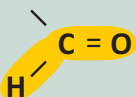
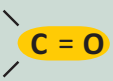
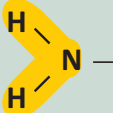
	HYDROCARBON DERIVATIVES	3
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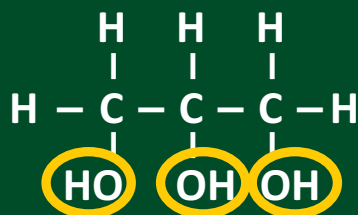
HYDROCARBON DERIVATIVES – COMPOUNDS OF CARBON, HYDROGEN AND SOMETHING ELSE

Many organic compounds may be considered as derivatives of hydrocarbons in whose molecules one or more H atoms have been replaced by other atoms, or atomic groups, called **substituents**. Such compounds are called **HYDROCARBON DERIVATIVES**. Their molecules are built up of carbon atoms, hydrogen atoms and atoms of at least one other element – most often halogen, oxygen, nitrogen. The properties of these compounds are highly dependent on the nature of the substituent (an atom, other than hydrogen, or a group of atoms).

The simplest hydrocarbon derivatives are their halogen derivatives (for example chloromethane CH_3Cl , tetrachloromethane CCl_4 , bromoethene $\text{C}_2\text{H}_5\text{Br}$, chlorobenzene $\text{C}_6\text{H}_5\text{Cl}$ etc.). If the substituent is a specific atomic group, called **FUNCTIONAL GROUP**, molecules are more complex. The chemical reactivity of these compounds is highly dependent on the functional groups. The major classes of hydrocarbon derivatives correspond to the major types of functional groups:

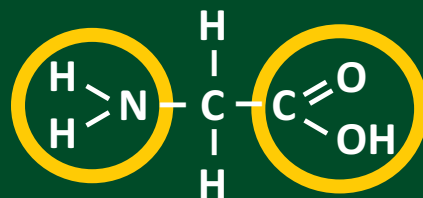
FUNCTIONAL GROUP					
	Hydroxy	Aldehyde	Ketone	Carboxyl	Amino
HYDROCARBON DERIVATIVES	ALCOHOLS	ALDEHYDES	KETONES	CARBOXYLIC ACIDS	AMINES

In the molecules of many organic compounds there are two or more functional groups (same or different). For example:



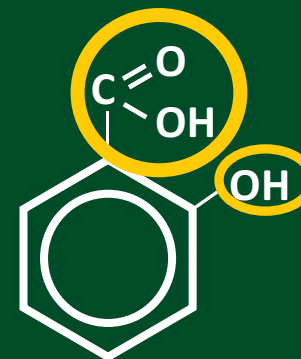
Glycerol

three **hydroxy** groups **-OH**



Glycine

one **amino** group **-NH₂**
one **carboxyl** group **-COOH**



salicylic acid

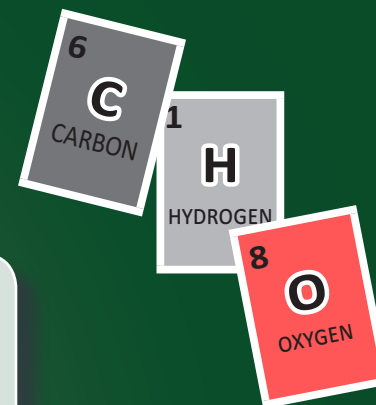
one **hydroxy** group **-OH**
one **carboxyl** group **-COOH**

Hydrocarbon derivatives are widely used – in the pharmaceutical industry and medicine, as components of perfumes compositions, in the food industry, the textile industry, for the production of plastics, dyes, varnishes etc.

33

HYDROXY DERIVATIVES

ALCOHOLS. PHENOLS

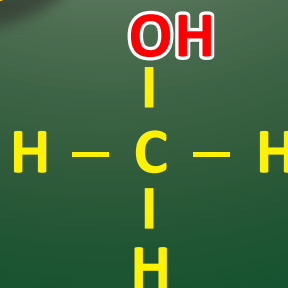
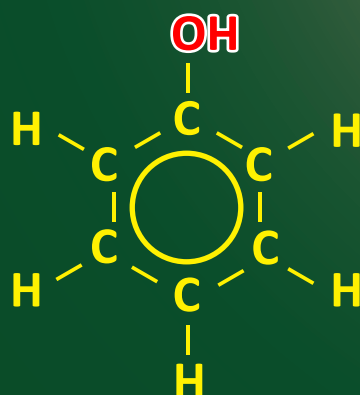


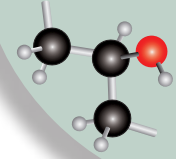
KEY TOPICS

1. What are alcohols?
2. What are phenols?
3. Why are alcohols and phenols hydrocarbon derivatives?
4. How to name alcohols?

KEY WORDS

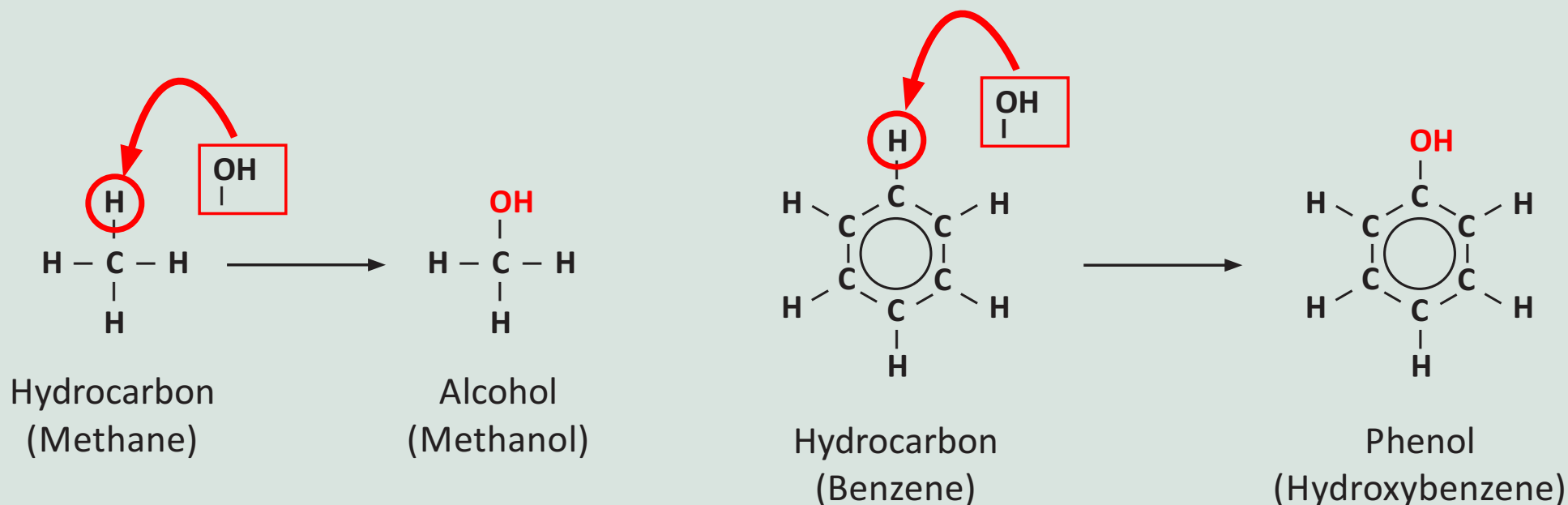
- Substituent
- Functional group
- Alcohol
- Phenol
- Monohydric alcohols
- Polyhydric alcohols
- Primary, Secondary, Tertiary alcohols

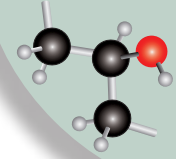




HYDROXY DERIVATIVES of hydrocarbons are composed of carbon, hydrogen and oxygen. In hydrocarbons molecules one or more hydrogen atoms have been replaced by **hydroxy groups –OH**. This is the functional group of this class of organic compounds.

The hydroxy derivatives of the aliphatic hydrocarbons are known as **alcohols** (in Arabian language means something fine), while those of the aromatic hydrocarbons in whose molecules the –OH group is bonded directly to the aromatic ring are called **phenols**:





ALCOHOLS ARE ORGANIC COMPOUNDS WITH ONE OR MORE –OH GROUPS BONDED TO CARBON ATOMS OF HYDROCARBON CHAINS.

The simplest alcohol is CH_3OH (methanol). The general formula of the straight chain monohydric (contain only one – OH group) saturated alcohol is $\text{C}_n\text{H}_{2n+1}\text{OH}$ ($\text{C}_n\text{H}_{2n+2}\text{O}$).

PROBLEM!

Express the molecular formulae of the hydroxy derivatives of ethane and pentane with one – OH group.

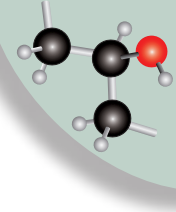
SOLUTION: 1. The hydroxy derivative of ethane C_2H_6 has 2 C atoms in its molecules and $n = 2$. From the general formula we calculate the number of hydrogen atoms bonded to these 2 C atoms:

$$2n + 1 = 2 \cdot 2 + 1 = 5 \text{ H atoms.}$$

2. The hydroxy derivative of pentane C_5H_{12} has a five carbon atoms chain and one –OH group in its molecules. So $n = 5$ and the number of H atoms in its molecule (except the H atom of the –OH group) is $5 \cdot 2 + 1 = 11$ H atoms.

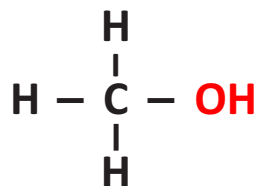
ANSWER: The molecular formula of the hydroxy derivative of ethane is $\text{C}_2\text{H}_5\text{OH}$.

The molecular formula of the hydroxy derivative of pentane is $\text{C}_5\text{H}_{11}\text{OH}$.

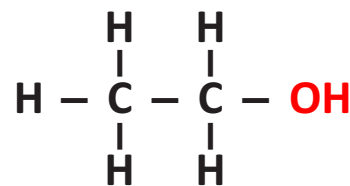


Depending on the number of the hydroxy groups in their molecules alcohols are classified as **monohydric** (with one –OH group) and **polyhydric** (with two or more –OH groups):

MONOHYDRIC ALCOHOLS

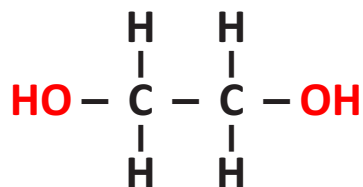


Methanol

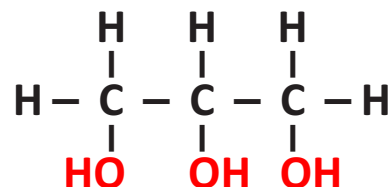


Ethanol

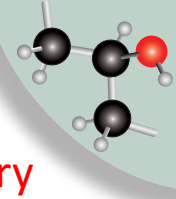
POLYHYDRIC ALCOHOLS



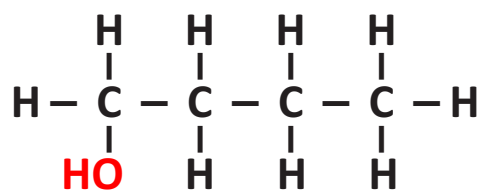
Ethane-1,2-diol



Propane-1,2,3-triol

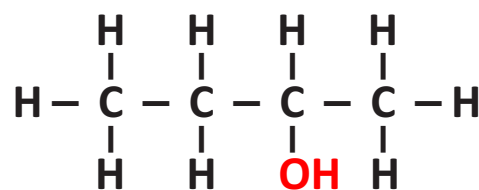


Alcohols are classified also as **primary** (the –OH group is bonded to a primary C atom), **secondary** (the –OH group is bonded to a secondary C atom) and **tertiary** (the –OH group is bonded to a tertiary C atom). For example:



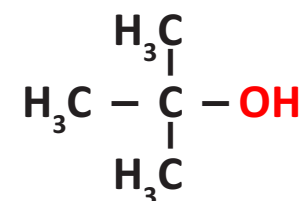
Butan-1-ol

Primary alcohol



Butan-2-ol

Secondary alcohol



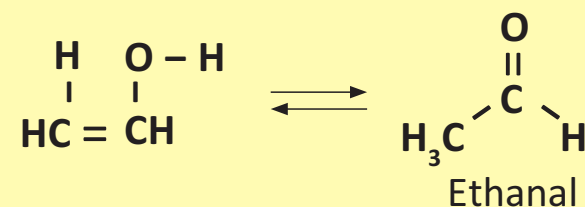
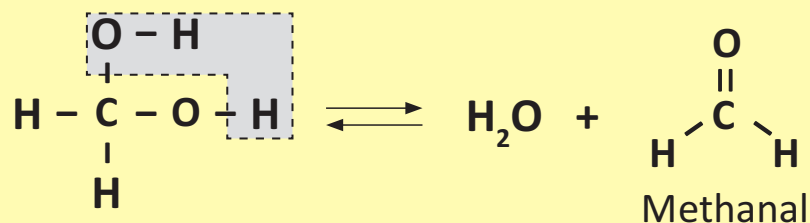
Methylpropan-2-ol

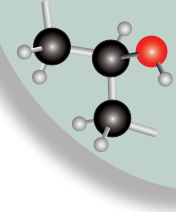
Tertiary alcohol

Note down that these alcohols are isomers because their molecular formulae are identical – $\text{C}_4\text{H}_{10}\text{O}$.

It is interesting to know:

Molecules with two –OH groups attached to the same carbon atom, as well as molecules with one –OH group attached to double bonded carbon atom, are unstable. They transform easily into more stable compounds:

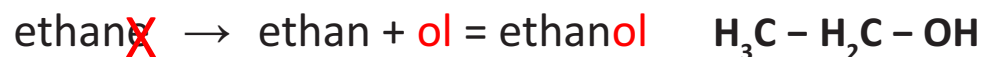
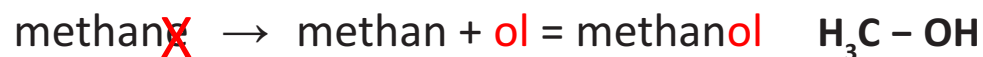




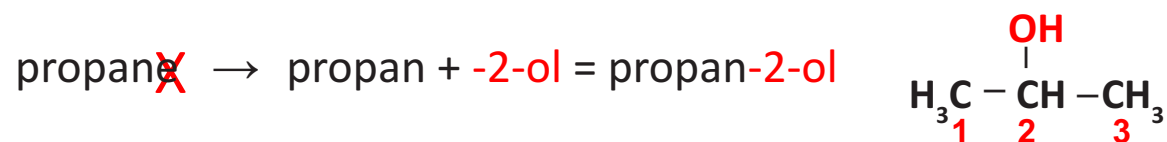
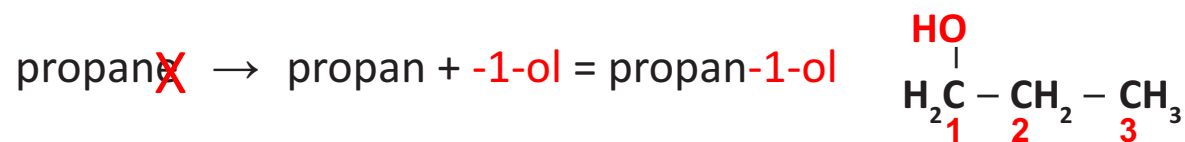
HOW TO NAME ALCOHOLS?

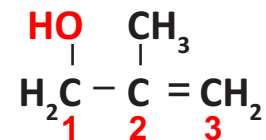
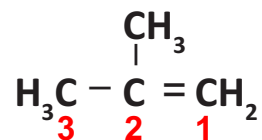
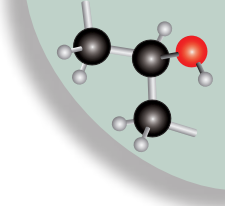
Alcohols are named according to some rules:

1. The parent hydrocarbon gives the name of the alcohol (the longest chain always includes the –OH group). The final „e“ is dropped and the suffix „-ol“ is added:



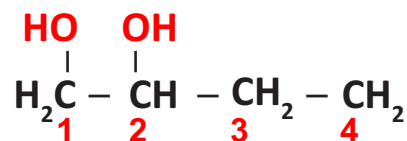
2. The place of the –OH group is indicated by the number of the carbon atom to which it is bonded, written after the parent hydrocarbon name and separated by dashes. The numbering of the carbon atoms always starts from the chain end nearest to the hydroxy group:



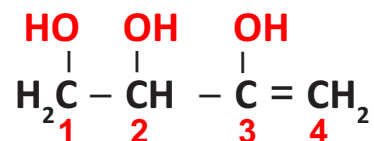


Note that the numbering of the C atoms in the hydrocarbon molecule and the alcohol molecule is not the same.

3. If there are two or more –OH groups this suffix „–ol“ is preceded by the prefixes „di–“ (if there are two –OH groups), „tri–“ (for three –OH groups) etc. For example:



Butane-1,2-diol



But-3-ene-1,2,3-triol

CAN YOU ANSWER THESE QUESTIONS ?

1. What are alcohols?
2. Why are alcohols and phenols different classes of hydroxy derivatives of hydrocarbons?
3. How is the alcohol $\text{C}_4\text{H}_9\text{OH}$ named?
4. Why is the alcohol name propan-3-ol wrong? What is the correct name?
5. How many hydroxy groups are there in the molecules of butanediol?
6. What types of isomers do alcohols with three or more carbon atoms have? Why?
7. Do you expect that alcohols are reactive compounds? Why?

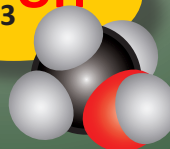
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METHANOL. ETHANOL ETHANE-1,2-DIOL. PROPANE-1,2,3-TRIOL

KEY TOPICS

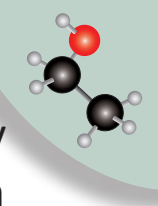
1. Why do methanol and ethanol display similar properties?
2. Why are methanol and ethanol perspective fuels?
3. What are the health hazards of the alcohol abuse?
4. Why is glycerol so important for the human metabolism?

– OH



KEY WORDS

- Methanol
- Ethanol
- Ethane-1,2-diol
- Propane-1,2,3-triol
- Esterification
- Nitroglycerine
- Triglycerides
- Biofuel

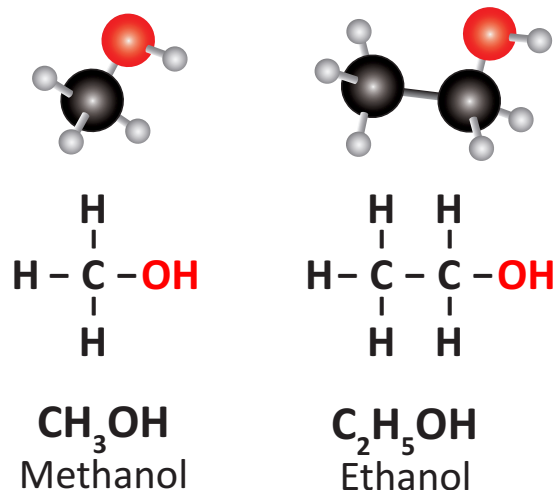


The simplest alcohols are **METHANOL CH_3OH** and **ETHANOL $\text{C}_2\text{H}_5\text{OH}$** . Ethanol is the most widely used alcohol. It is known from ancient times but pure ethanol was first prepared in the late XVIIIth century. Its common names are simply **alcohol**, **drinking alcohol**, **ethyl alcohol** and is found in all alcoholic beverages. Methanol is also known as **wood alcohol**.

Methanol and ethanol are monohydric alcohols – they have only one -OH group in their molecules.

ETHANE-1,2-DIOL and **PROPANE-1,2,3-TRIOL** are one of the simplest polyhydric alcohols. They are commonly called **glycol** (or **ethylene glycol**) and **glycero/** (or **glycerine**). In both compounds the -OH groups are bonded to different carbon atoms.

PHYSICAL PROPERTIES

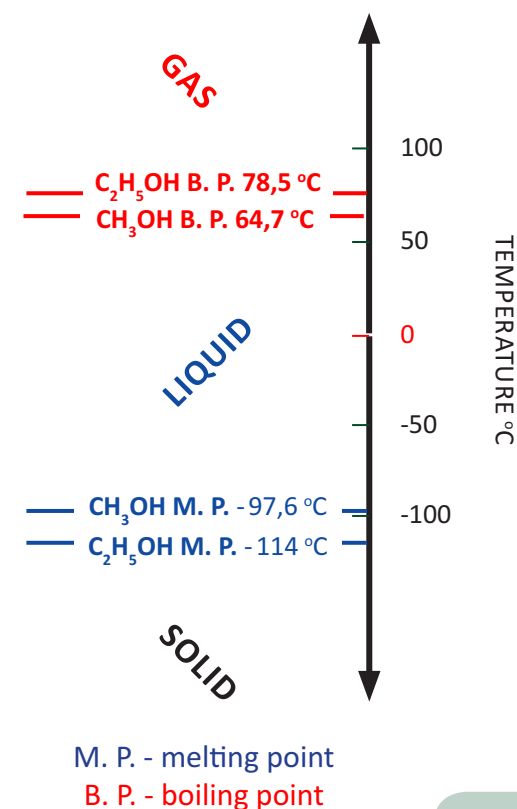


Methanol CH_3OH and ethanol $\text{C}_2\text{H}_5\text{OH}$ are colourless, volatile, flammable liquids. Ethanol has a pungent taste and a characteristic vinous odour, while methanol has a distinctive odour and is sweeter than ethanol.

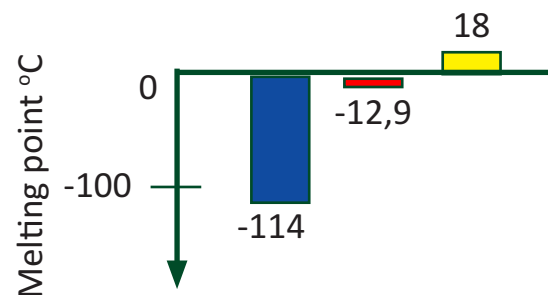
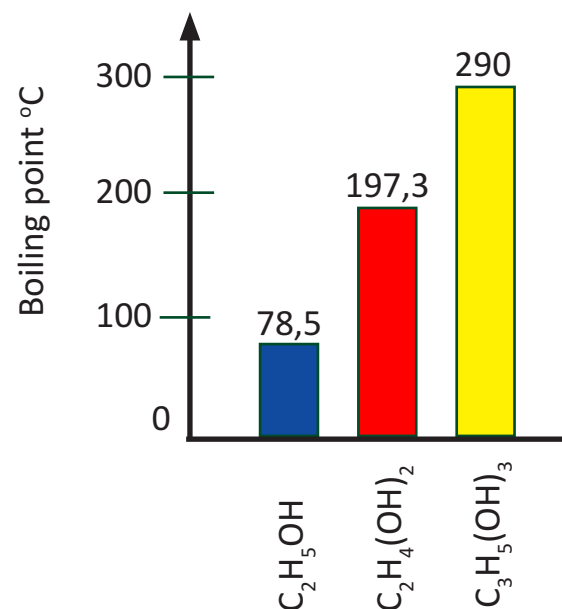
Both methanol and ethanol are lighter than water and dissolve in it. The content of ethanol, expressed in volume percentages, is called **alcoholic strength by volume**. For example there

are 12 ml of pure ethanol in 100 ml of wine with alcoholic strength by volume 12 % vol. Methanol and ethanol are good solvents of many compounds.

Methanol is toxic. If ingested it can cause blindness.

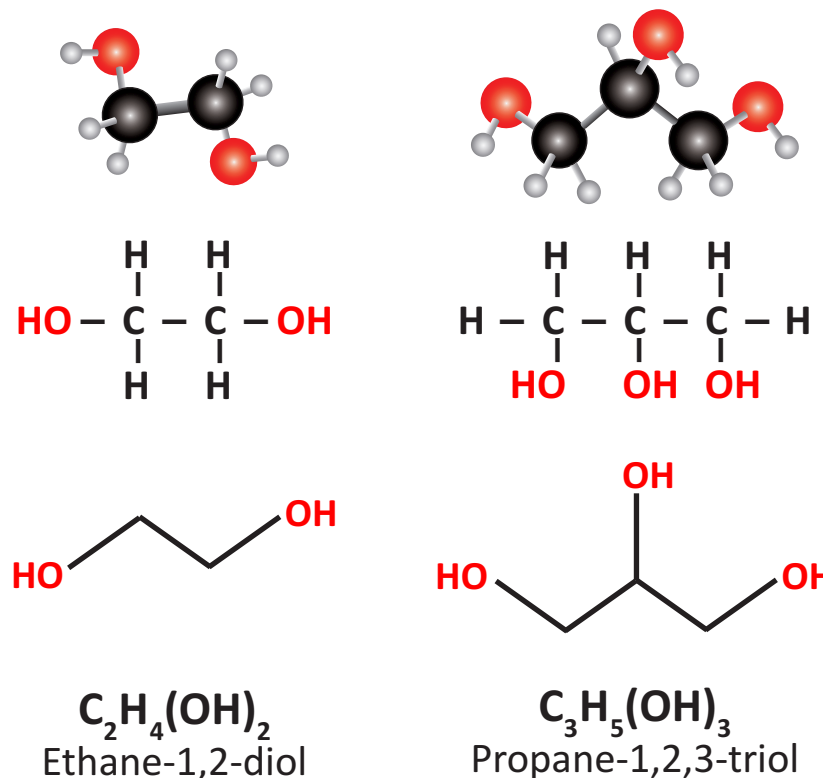


Ethane-1,2-diol and propane-1,2,3-triol are colourless, odourless liquids, look like syrups, sweet

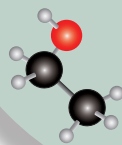


(their common names originate from the Greek word „glyceros“ meaning sweetish) and dissolve easily in water. But it is dangerous to confuse them as glycerol is a food sweetener while glycol is a poison.

Both alcohols are heavier than water (unlike methanol and ethanol which are lighter). Because of the presence of two or three –OH groups their melting and boiling points are relatively high. At 18 °C or less glycerol is solid. It is highly hygroscopic and can burn the skin.



Methanol, ethanol, etane-1,2-diol and propane-1,2,3-triol display some similar properties as all four alcohols have the same functional group –OH in their molecules. But there are some differences in their chemical properties resulting from the different number of hydroxy groups in their molecules.



CHEMICAL PROPERTIES

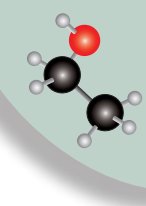
The chemical activity of alcohols is strongly affected by the presence of the –OH functional group. Both O – H and C – O bonds are covalent polar bonds and can be broken down.

DISRUPTION OF THE O – H BOND

Interaction with active metals. As the O – H bond is polar active metals easily substitute the hydrogen atom in the hydroxy group. For example in the reaction of ethanol with sodium the products are sodium ethoxide and hydrogen:

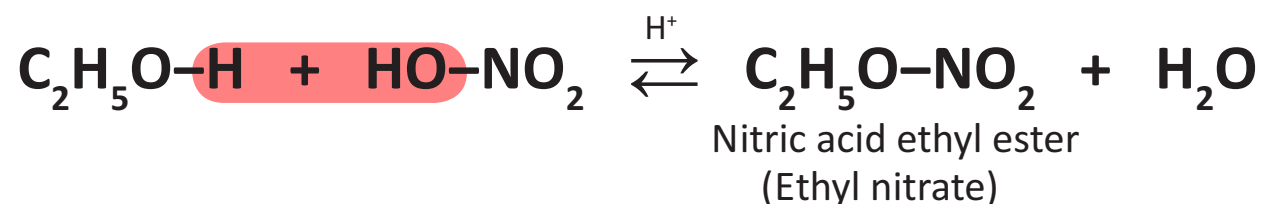


Ethanol and methanol slightly dissociate in water (even less than water). The concentration of H^+ (H_3O^+) ions is very low and they cannot be considered as acids – the blue litmus does not turn red.



Interaction with oxy-acids. In these reactions the hydrogen of the hydroxy group is replaced by a positive acidic ion. For example NO_2^+ if nitric acid HNO_3 is used.

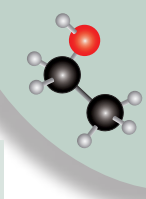
For instance the reaction of the concentrated nitric HNO_3 acid with ethanol:



This reaction is catalysed* by H^+ ions. The process is *molecular, slow and reversible*. This is a reaction of **ESTERIFICATION**. The products are an **ester** and water:

**THE REACTION OF AN ALCOHOL WITH AN OXY-ACID,
YIELDING AN ESTER AND WATER,
IS CALLED **ESTERIFICATION**.**

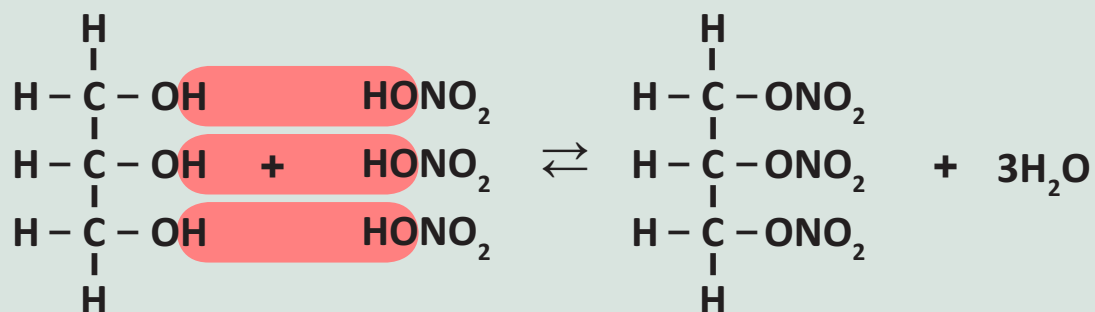
* **Catalysts** are substances that accelerate chemical reactions without themselves being consumed.



PROBLEM!

How many molecules of nitric acid HNO_3 react with 1 molecule of propane-1,2,3-triol?

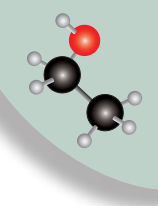
SOLUTION: There are three hydroxy groups in the propane-1,2,3-triol molecule. Each of them reacts with 1 nitric acid molecule. The chemical equation of the reaction (it would be more clear if structural formulae are used) is:



ANSWER: 1 propane-1,2,3-triol molecule reacts with 3 molecules of HNO_3 .

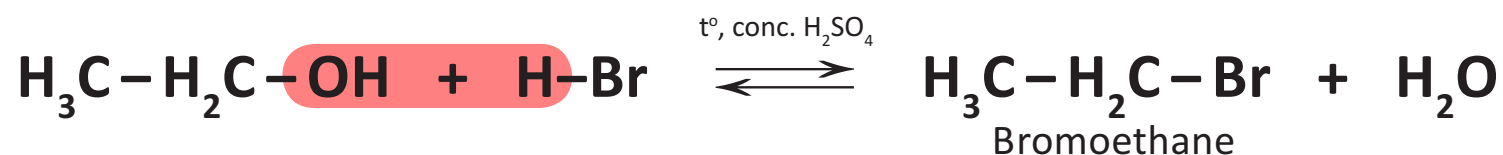
This reaction was discovered by Ascanio Sobrero in the mid XIXth century. The nitric acid ester of propane-1,2,3-triol (glycerine) is commonly known as nitroglycerine – a colourless viscous liquid that explodes on impact and is an active ingredient of the dynamite. Nitroglycerine (tablets, ointments, solutions, sprays) is used as a medicine for some heart diseases.

Blue litmus does not turn red in aqueous solutions of ethane-1,2-diol and propane-1,2,3-triol (as for ethanol).



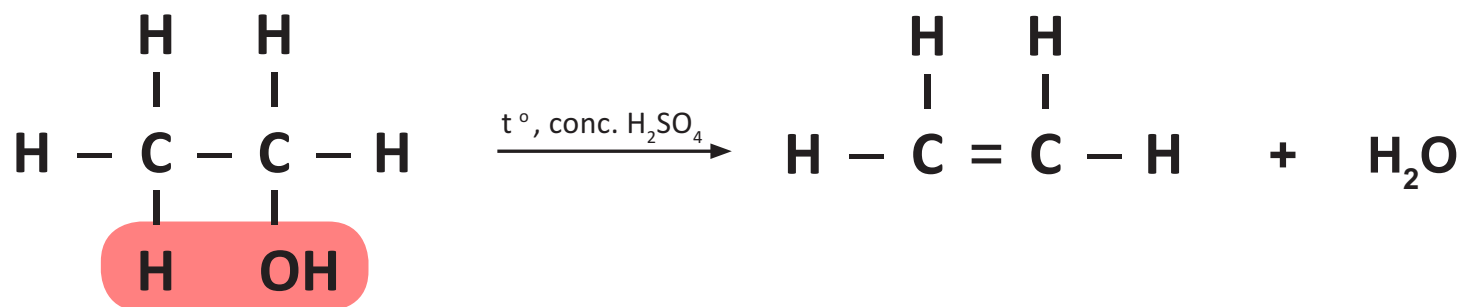
DISRUPTION OF THE C–O BOND

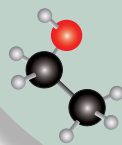
Interaction with hydrogen halides. The products are halogen derivatives of the corresponding hydrocarbons and water. For example:



The water is formed by the ethanol –OH group and the hydrogen of the hydrogen halide

Dehydration (loss of a water molecule). The reaction is catalytic and undergoes at high temperature. Ethanol is converted into ethene and water is liberated:





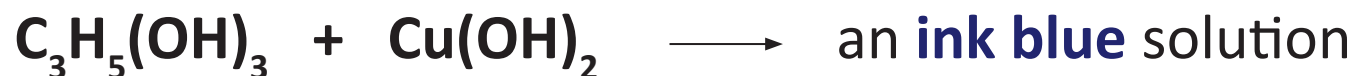
TEST REACTIONS FOR ALCOHOLS

If a iodine solution is added to ethanol, followed, under heating, by a solution of NaOH, after a few minutes an yellow precipitate of triiodomethane CHI_3 (iodoform), smelling as an „antiseptic“, appears.

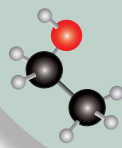
! The reaction with iodine I_2 in the presence of sodium hydroxide NaOH is a test reaction for ethanol.

If methanol CH_3OH is used instead of ethanol no reaction occurs. This could be a test to distinguish between methanol and ethanol. That might be very important as methanol looks like ethanol, but it is a poison and can cause blindness or even may be fatal if ingested.

Polyhydric alcohols as ethane-1,2-diol and propane-1,2,3-triol react with $\text{Cu}(\text{OH})_2$. The solution turns ink-blue:



! The interaction with copper dihydroxide $\text{Cu}(\text{OH})_2$ (freshly precipitated) is a test reaction for all polyhydric alcohols.



COMBUSTION

The products of the complete combustion of alcohols are CO₂ and water vapours. For example:



Energy is in the form of light (pale not smoky flame) and a considerable amount of heat. Ethanol is a renewable **biofuel** (it is produced from plant biomass in a short period of time). To burn efficiently ethanol must be aerosolized.

The use of methanol and ethanol as fuels contribute to the reduction of greenhouse gases emissions as from 1 mole of methanol is produced only 1 mole of CO₂ and from 1 mole of ethanol – 2 moles of CO₂. Ethanol and biodiesel are the two most widely used biofuels.

In the laboratory ethanol is used as a fuel in the alcohol burners. This ethanol and the ethanol for domestic uses is denaturated – it is made undrinkable by the addition of some compounds (denaturants), which usually have an unpleasant odour.

PRODUCTION

On an industrial scale methanol CH_3OH is produced using natural gas as a feedstock. But CH_3OH can be synthesised also from carbon monoxide or carbon dioxide (even from air) and hydrogen:



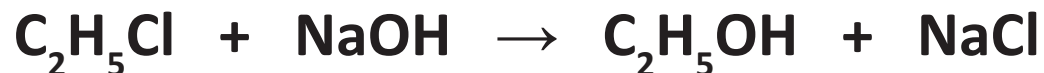
A well known method to produce ethanol is the **ethanol (or alcoholic) fermentation**. This is a biochemical process in which glucose $\text{C}_6\text{H}_{12}\text{O}_6$ is transformed into ethanol and carbon dioxide. The process is catalyzed by the enzyme zymase:



The raw material are fruits, cereals (barley, rice, wheat, corn etc.), sugar beet.

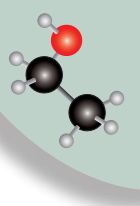
On an industrial scale ethanol is produced from ethene (the most important petrochemical product). (hydration of ethene, see p. 48 chap. V. Hydrocarbons).

In the laboratory a small amount of ethanol may be prepared in the reaction of an ethyl halide (for example $\text{C}_2\text{H}_5\text{Cl}$) with a strong base (for example NaOH):



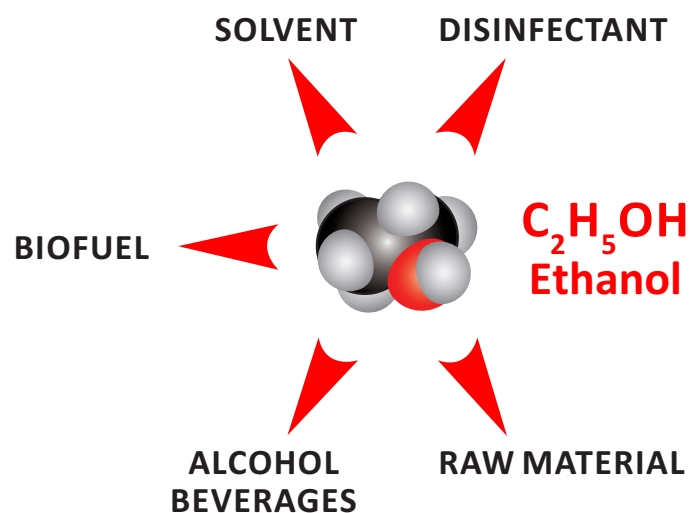
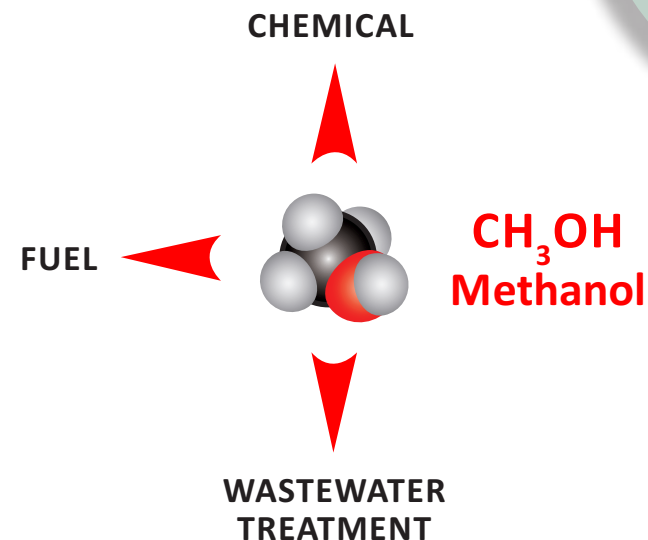
Carl Wilhelm Scheele first isolated propane-1,2,3-triol (glycerol) in the second half of XVIIIth century – in a reaction of fats with NaOH (a process called saponification) he produced glycerol and soaps.

On an industrial scale ethane-1,2-diol (glycol) and propane-1,2,3-triol (glycerol) are petrochemical products. Glycerol is produced from propene (see the problem in your Study book). Glycol is produced from ethene.



USES

Methanol CH_3OH is one of the most widely used industrial chemicals. It is a key chemical to manufacture formaldehyde and acetic acid in chemical synthesis. It is used as an antifreeze and as a solvent. Methanol is also a fuel and is used for wastewater treatment. The worldwide production of methanol exceeds 130 billions litres annually.



Ethanol $\text{C}_2\text{H}_5\text{OH}$ is a widely used organic compound. It is a raw material to synthesize ethanoic (acetic) acid, esters, amines etc. Ethanol is a very good solvent of many compounds and is used to prepare tinctures (the Iodine bought in a pharmacy is in fact a solution of the crystal I_2 in ethanol), perfume compositions, varnishes. Ethanol is also a disinfectant as the proteins structure dramatically changes under its action – if you put the egg white in a bowl and add a few ml of ethanol, you will see soon that the egg white darkens.

Ethanol is a biofuel.

All alcoholic beverages contain ethanol. It becomes an intoxicating agent if a person consumes more alcohol than the organism can metabolise. Cardiovascular diseases, cancer, irreversible damage of the nervous system, depression, antisocial personality disorder are inevitable after a long-term alcohol misuse. Drinking alcohol and driving is absolutely irresponsible and is prosecuted by the law.



Ethane-1,2-diol (glycol) is miscible with water in any proportions. The 50 % solution freezes at $-34\text{ }^{\circ}\text{C}$ and is widely used in the cars engine cooling systems (antifreeze) to lower the freezing point of the water. It also increases the coolant boiling point thus preventing it from overheating. Glycol is also used for the production of polymers – for example polyethylene terephthalate (basic component of polyester fibres and plastics used worldwide to package foods).

Propame-1,2,3-triol (glycerol) is widely used in the food industry, the cosmetic industry (it is added to tooth pastes, ointments, soaps to prevent them from drying as it does not irritate the skin and is a good humectant), the production of plastics, explosives, fibres, also sometimes as an antifreeze, in the tobacco industry, the leather industry.

Propame-1,2,3-triol play an important role for the body functioning because fats are esters of propane-1,2,3-triol and high molecular weight carboxylic acids. The content of fats (called triglycerides) in the blood is an indicator of the risk of heart attack and stroke. So it is very important to maintain an optimum level of triglycerides in the blood.

CAN YOU ANSWER THESE QUESTIONS ?

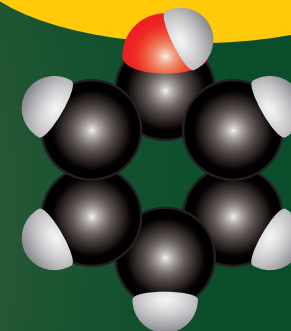
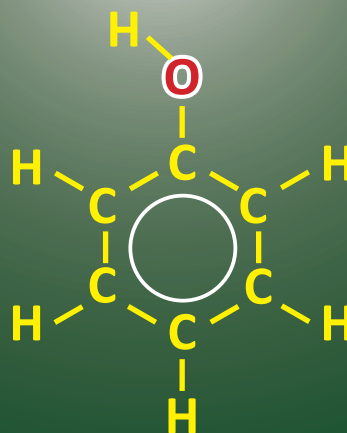
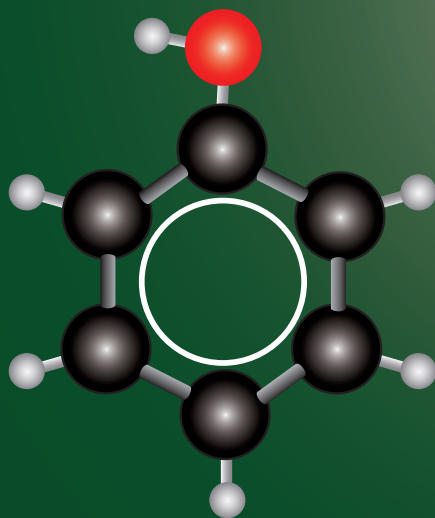
1. Why is ethanol highly soluble in water, while ethane is insoluble?
2. Why does ethane-1,2-diol boil at a higher temperature than ethanol?
3. Can you propose three methods to prepare ethanol?
4. In a test tube containing 5 ml of water are added carefully 5 ml of ethanol. Two layers are formed as ethanol is lighter than water. They disappear after gently shaking the test tube. The liquid temperature slightly increases and the volume shrinks. Why?
5. Why does not the blue litmus turn red in aqueous solutions of ethane-1,2-diol and propane-1,2,3-triol?
6. How to prepare the $\text{Cu}(\text{OH})_2$ used in the test reaction for polyhydric alcohols?
7. How to distinguish between ethane-1,2-diol and propane-1,2,3-triol?
8. What is common between propane-1,2,3-triol and dynamite?
9. Why is it very dangerous to taste the antifreeze?
10. What does propane-1,2,3-triol have to do with human health?
- 11 Why is short term and long term alcohol abuse a health disaster?

35

PHENOL (BENZENOL)

KEY TOPICS

1. Why is phenol the simplest aromatic alcohol?
2. Why is phenol an acid?
3. Why is phenol more reactive than benzene?



KEY WORDS

- Benzenol
- Phenol
- Carboic acid
- Picric acid



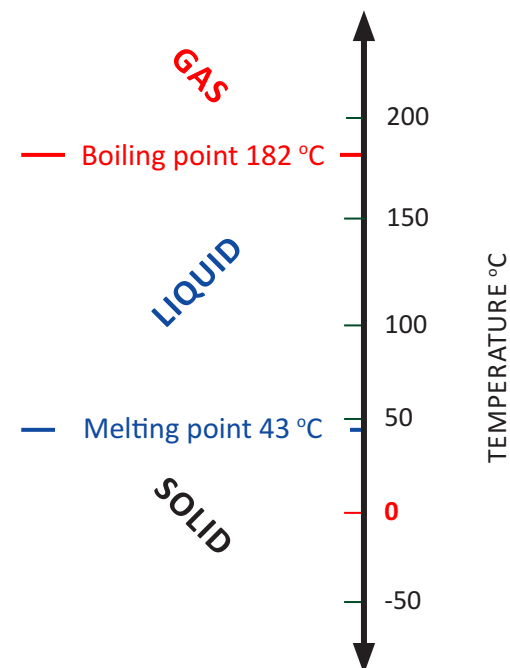
Polarity of the -OH bond in the phenol molecule

PHENOL $\text{C}_6\text{H}_5\text{OH}$, also known as **BENZENOL** (also *hydroxybenzene* or *carbolic acid*) is a monohydric derivative of benzene C_6H_6 – one hydrogen atom bonded to a carbon atom of the aromatic ring has been replaced by a hydroxy group -OH. Owing to the interaction of one of the lone electron pairs of the oxygen of the hydroxy group with the delocalized electrons of the aromatic ring the O – H bond is more polarized than the O – H bond in the alcohol molecules.

PHYSICAL PROPERTIES

Phenol is a colourless crystalline solid with a specific odour. It is easily oxidized by the oxygen in the air and its colour turns pink. It melts at 43°C and boils at 182°C . Phenol is completely miscible with hot water. In cool water it is only slightly soluble. The diluted aqueous solution of phenol is used as disinfectant.

PHENOL IS POISONOUS. MAY CAUSE SEVERE SKIN BURNS AND IS TOXIC (ITS VAPOURS MUST NOT BE INHALED).





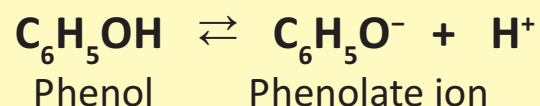
It is interesting to know:

CHEMICAL PROPERTIES

Typical for phenol are reactions involving the functional hydroxy group –OH or the aromatic ring:

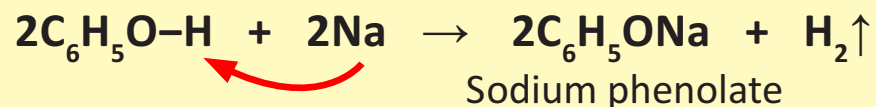
REACTIONS OF THE –OH GROUP:

As the O – H bond in the hydroxy group of phenol is more polarized than the O – H bond in the alcohols molecules, phenol *partially dissociates* in water into positive hydrogen ions H^+ and negative **phenolate** ions $\text{C}_6\text{H}_5\text{O}^-$:



Thus blue litmus turns red in aqueous solutions of phenol – phenol is a weak acid. Its aqueous solution (**carbolic acid**) has been one of the first antiseptics used in surgery.

Dissolved in water phenol reacts with *active metals* and their *bases*, yielding salts (called *phenolates*) and gaseous hydrogen:

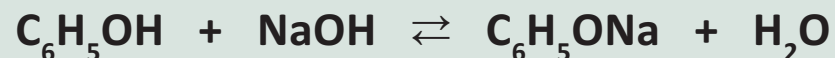




PROBLEM!

How many moles of water are formed in the reaction of 5 moles of phenol $\text{C}_6\text{H}_5\text{OH}$ with 5 moles of sodium hydroxide NaOH ?

SOLUTION: The balanced chemical equation of the reaction is:



From the incomplete molar ratio $n(\text{C}_6\text{H}_5\text{OH}) : n(\text{NaOH}) : n(\text{H}_2\text{O}) = 1 : 1 : 1$ we have $n(\text{H}_2\text{O}) = n(\text{C}_6\text{H}_5\text{OH}) = n(\text{NaOH})$.

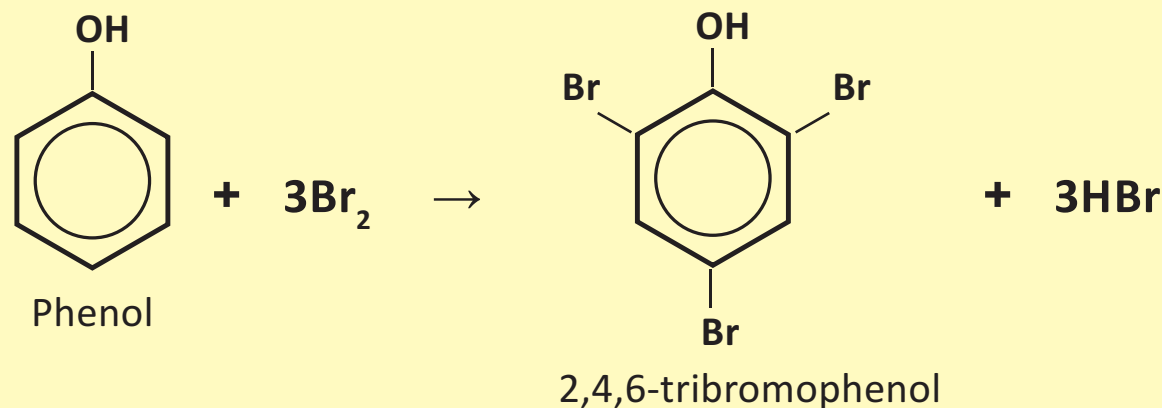
So for $n(\text{C}_6\text{H}_5\text{OH}) = n(\text{NaOH}) = 5$ moles we obtain $n(\text{H}_2\text{O}) = 5$ moles.

ANSWER: In the reaction of 5 moles of phenol $\text{C}_6\text{H}_5\text{OH}$ with 5 moles of sodium hydroxide NaOH 5 moles of water are formed.

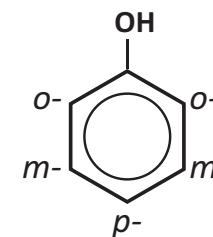


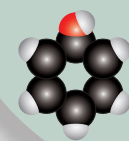
REACTIONS OF THE AROMATIC RING

Phenol reacts with *halogens* and *strong acids* (for example HNO_3). The reactions are easy as compared to benzene because the hydroxy group makes the aromatic ring more reactive than it is in the benzene molecule. As a result the reaction with bromine water undergoes without any catalyst and heating, yielding a white precipitate of crystalline 2,4,6-tribromophenol (the $-\text{OH}$ group directs the substituents to *ortho*- and *para*- positions^{*}):

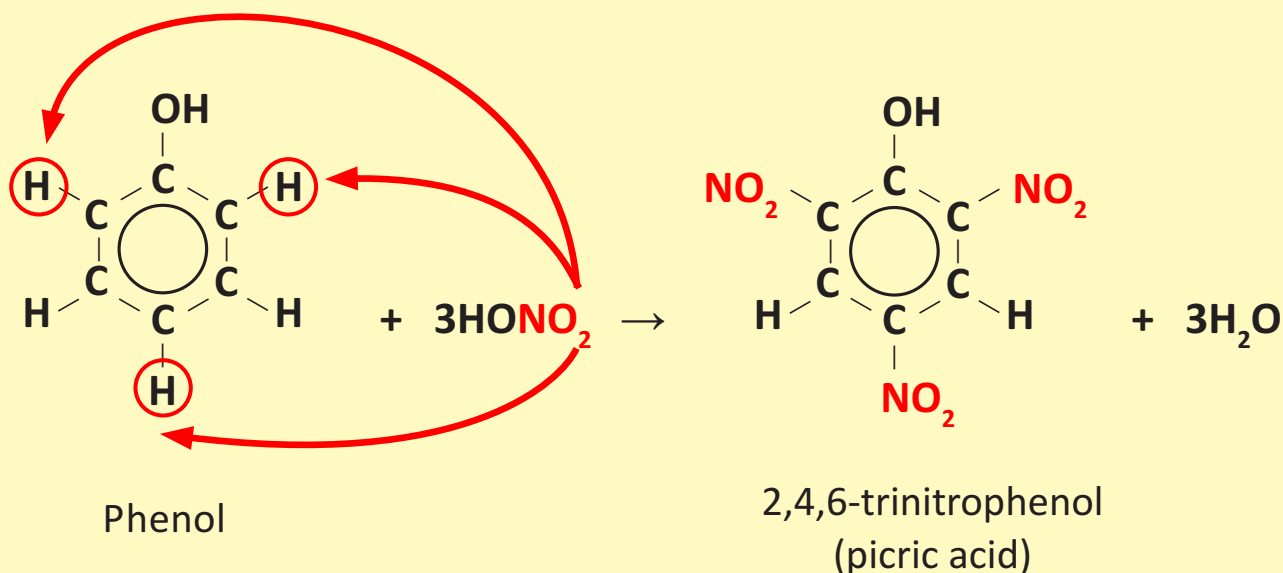


^{*}The place of the substituents is indicated by the symbols: *o*- (abbreviation of „ortho“), *m*- (abbreviation of „meta“) and *p*- (abbreviation of „para“):



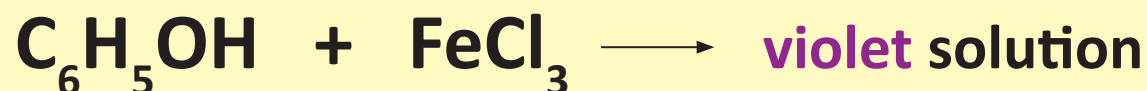


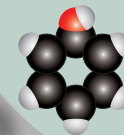
In the reaction with dilute nitric acid (it is not necessary to use concentrated acid or to mix it with concentrated H_2SO_4 as it is for benzene) hydrogen atoms on *orto*- and *para*- positions are substituted by NO_2^+ ions and water is released:



The product of the reaction 2,4,6-trinitrophenol (TNP) is commonly called *picric acid*. It is a crystalline substance easily exploding on impact or friction.

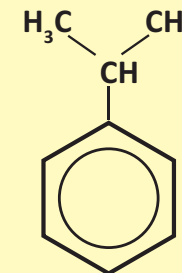
! The interaction with aqueous solution of FeCl_3 is a test reaction for phenol.
The solution turns violet:





PRODUCTION

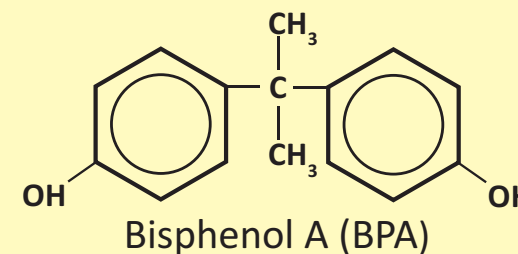
A common industrial method to produce phenol is the oxidation of 2-phenylpropane (or isopropylbenzene commonly called *cumene*). Propanone (known as acetone is a by-product). In the laboratory phenol may be prepared in a substitution reaction involving chlorobenzene and sodium hydroxide – look at your Study book.



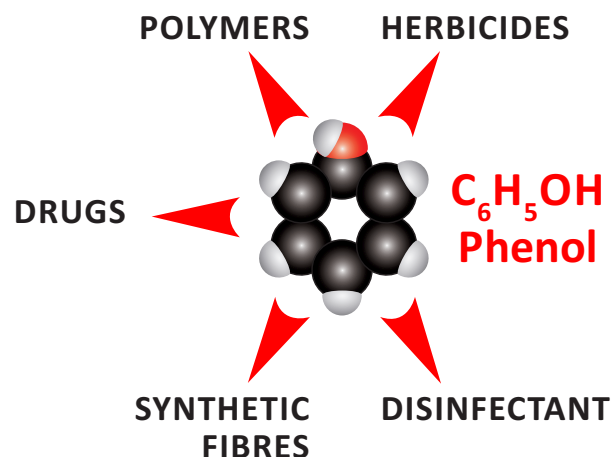
2-phenylpropane

USES

The annual world production of phenol is about 10 millions of tonnes. It is mainly used as a start material to produce bisphenol A (BPA used in the production of plastics and epoxy resins), phenolic resins, cyclohexanol also synthetic fibres, drugs and others.



Bisphenol A (BPA)



Phenol is a common water and soil pollutant. It and others phenols may be released to the environment (in industrial processes, use of products such as disinfectants, from cigarettes, vehicle emissions and many others) and may affect the brain, the heart, the skin etc. Thus the development of the so called green phenol technologies is a key factor for safeguarding the environment.

CAN YOU ANSWER THESE QUESTIONS ?

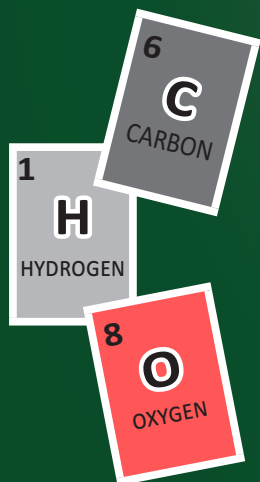
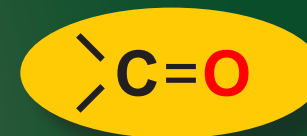
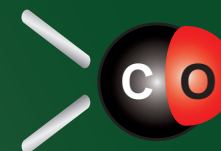
1. What names of the compound $\text{C}_6\text{H}_5\text{OH}$ do you know?
2. The melting and boiling points of methylbenzene $\text{C}_6\text{H}_5\text{CH}_3$ (-95°C and 111°C respectively) are lower than those of phenol. Why?
3. Why is phenol a weak acid while ethanol displays acid-base properties?
4. How to distinguish between ethanol and an aqueous solution of phenol?
5. Why is phenol harmful for man and for the environment?

36

ALDEHYDES. METHANAL. ETHANAL

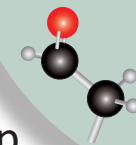
KEY TOPICS

1. What is a carbonyl group?
2. What are aldehydes?
3. How to name aldehydes?
4. Are aldehydes reactive compounds?



KEY WORDS

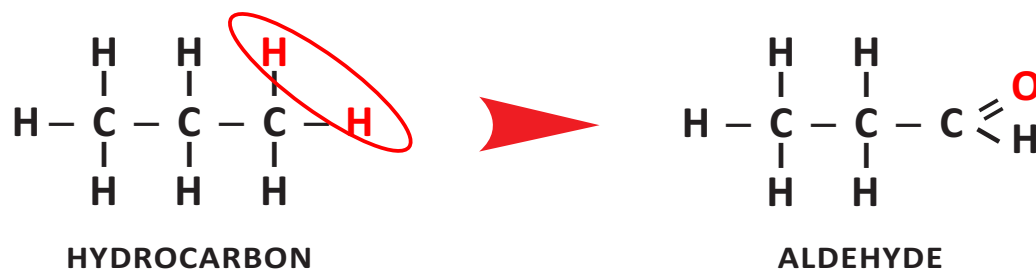
- Carbonyl group
- Aldehyde
- Aldehyde group
- Methanal
- Ethanal
- Silver mirror test
- Polyformaldehyde
(Polyoxymethylene POM)



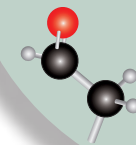
The atomic group >C=O (double bonded carbon and oxygen atoms) is a major functional group in the molecules of organic compounds as it is essential to their chemical activity. It is called **carbonyl group**. Organic compounds considered as derivatives of hydrocarbons in whose molecules two H atoms, bonded to the same C atom, have been substituted by a double bonded oxygen atom are called **carbonyl derivatives** of hydrocarbons. They always have at least one carbonyl group in their molecules.

The carbon atom of the carbonyl group can be an „end“ atom – two hydrogen atoms bonded to a primary carbon atom have been replaced by a double bonded oxygen atom. The carbonyl group is at the end of the carbon chain and its carbon atom is always covalently bonded to a hydrogen atom.

This „end“ carbonyl group O=C<H is called **aldehyde group**. In condensed structural formulae it is always expressed as **-CHO** (not -COH to not be confused with alcohols and phenols). Organic compounds with aldehydes groups in their molecules are called **ALDEHYDES**:



ALDEHYDES ARE ORGANIC COMPOUNDS WITH ALDEHYDES GROUPS O=C<H IN THEIR MOLECULES.



HOW TO NAME ALDEHYDES?

Aldehydes systematic names are formed following the same rules as for alcohols, but the added suffix is „-**al**“ (the final „e“ of the alkane name is dropped):

methan~~e~~ → methan + **al** = methan**al** HCHO

ethan~~e~~ → ethan + **al** = ethan**al** $\text{H}_3\text{C} - \text{CHO}$

Remember that **to the carbon atom of the aldehyde group always is assigned the number 1.**

ALDEHYDES	
CONDENSED FORMULA	NAME
$\text{H} - \text{C} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{H} \end{smallmatrix}$	methan al
$\text{H}_3\text{C} - \text{C} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{H} \end{smallmatrix}$	ethan al
$\text{H}_3\text{C} - \text{H}_2\text{C} - \text{C} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{H} \end{smallmatrix}$	propan al

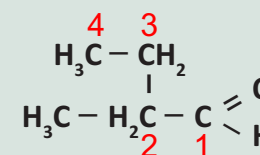
PROBLEM!

Name the aldehyde: $\begin{array}{c} \text{H}_3\text{C} - \text{CH}_2 \\ | \\ \text{H}_3\text{C} - \text{H}_2\text{C} - \text{C} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{H} \end{smallmatrix} \end{array}$

SOLUTION: 1. Determine the longest carbon chain that contains the aldehyde group and number the carbon atoms:

2. The main chain gives the name of the aldehyde – this is a branched butanal.

3. Name the branch chain: 2-methyl



ANSWER: The name of the compound is **2-methylbutanal**.

Methanal **HCHO** and ethanal **CH₃CHO** are the simplest aldehydes. They are better known with their common names – *formaldehyde* and *acetaldehyde*.

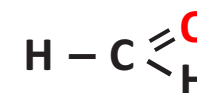
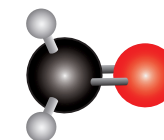
METHANAL HCHO. ETHANAL CH₃CHO

PHYSICAL PROPERTIES

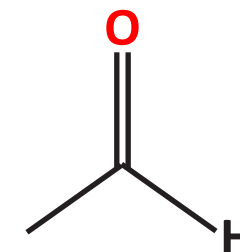
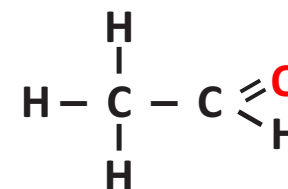
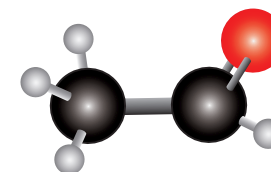
Methanal HCHO is one of the few organic compounds with only one C atom in its molecules. At standard conditions it is a colourless gas while ethanal **CH₃CHO** is a colourless liquid. As the

COMPOUND	Condensed formula	Relative molecular mass	Boiling point °C	Melting point °C
propane	CH ₃ CH ₂ CH ₃	44	– 42	– 188
ethanal	CH ₃ CHO	44	21	– 121
ethanol	CH ₃ CH ₂ OH	46	78,5	– 114

Methanal is a poison with a specific sharp, irritating odour. It is soluble in water. Its 37 % aqueous solution is known as *formalin*. It is used as a disinfectant, a preservative for biological specimens, etc. Ethanal is also soluble in water and has a sharp odour too.



Methanal
CHO



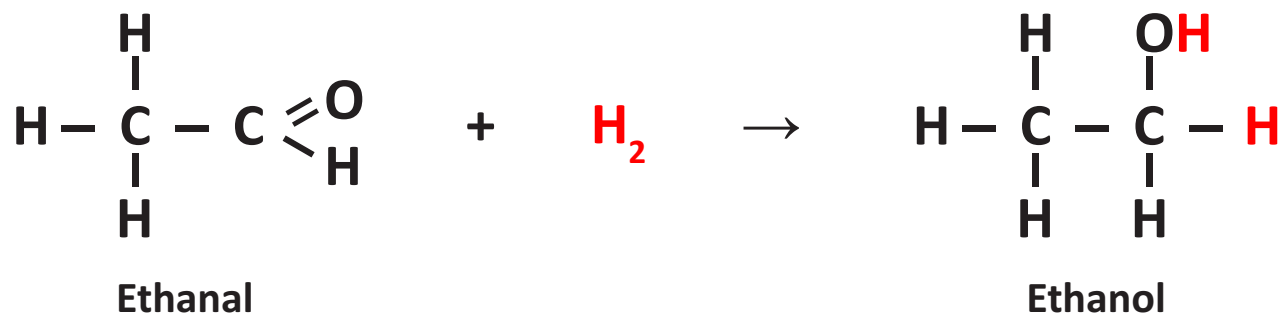
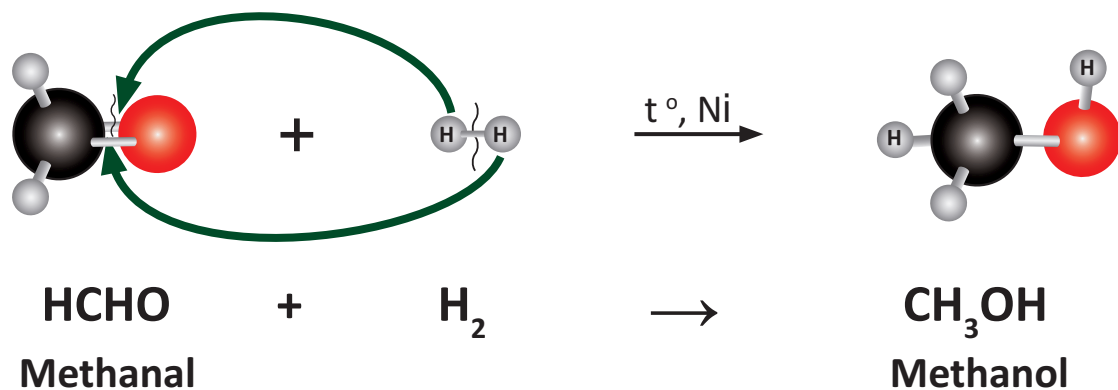
Ethanal
CH₃CHO

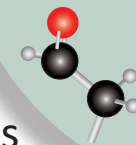
the C=O bond is polar their melting points (–92 °C for methanal and –121 °C for ethanal) and boiling points (–21 °C for methanal and 21 °C for ethanal) tend to be high compared to that of alkanes with a similar molecular mass. But they are low compared to the alcohols with the same number of carbon atoms.

CHEMICAL PROPERTIES

Typical for methanal and ethanal are reactions involving the aldehyde group -CHO .

Addition of hydrogen H_2 . Under heating and in the presence of a catalyst (nickel Ni) one of the bonds of the double C=O bond breaks down and two H atoms are added to each molecule. The product is the alcohol with the same number of carbon atoms (for example methanol if methanal reacts):

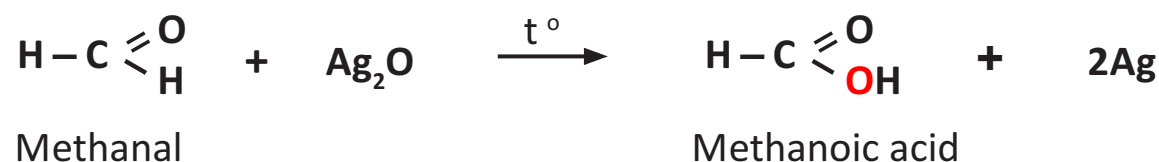




Reaction with Ag_2O and $\text{Cu}(\text{OH})_2$. The hydrogen of the aldehyde group is very mobile and the aldehydes easily transform into compounds known as carboxylic acids – an oxygen atom is „inserted“ between the carbon and the hydrogen atoms of the aldehyde group. If methanal reacts methanoic acid HCOOH is produced and if ethanal reacts – ethanoic acid CH_3COOH .

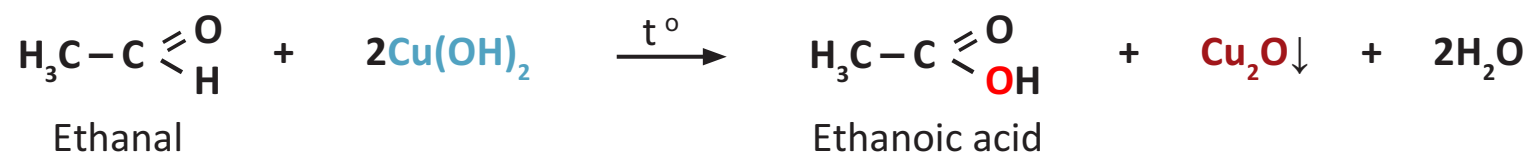
Typical are the reaction with Ag_2O and $\text{Cu}(\text{OH})_2$ but aldehydes transform into carboxylic acids even reacting with oxygen in the air.

In the reaction **with Ag_2O** (ammonia solution of Ag_2O known as Tollens' reagent) metallic silver is also produced. It is disposed on the test tube walls:



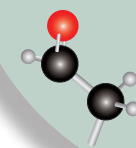
This reaction is known as **silver mirror test**.

In the reaction **with $\text{Cu}(\text{OH})_2$** (freshly precipitated, known as Fehling's solution)) a brick-red precipitate of Cu_2O is produced:

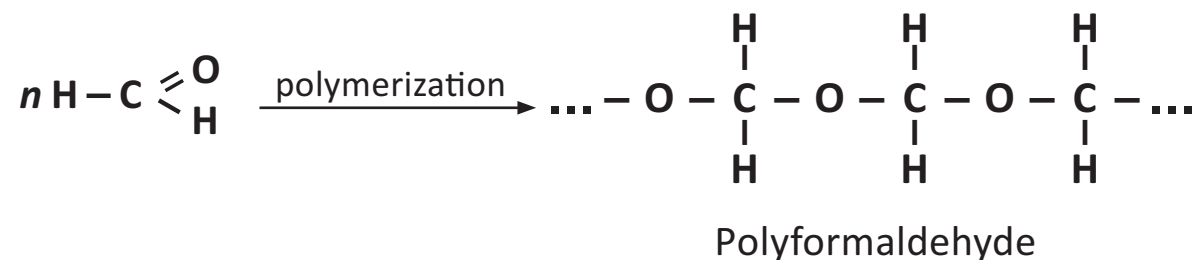


Both reactions take place under heating.

! The reactions with Ag_2O (an ammonia solution) and freshly precipitated $\text{Cu}(\text{OH})_2$ are test reactions for aldehydes.

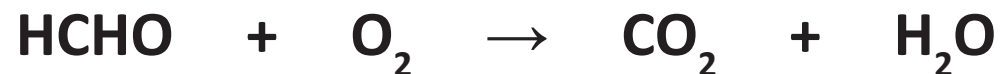


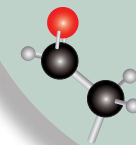
Polymerization. Owing to the disruption of one of the C=O bonds methanal easily polymerizes:



This polymer is a crystalline substance and has oxygen atoms along with carbon atoms in the main chain. Polyformaldehyde plastics are rigid and with a high mechanical strength. They are commonly known as POM (polyoxymethylene) plastics.

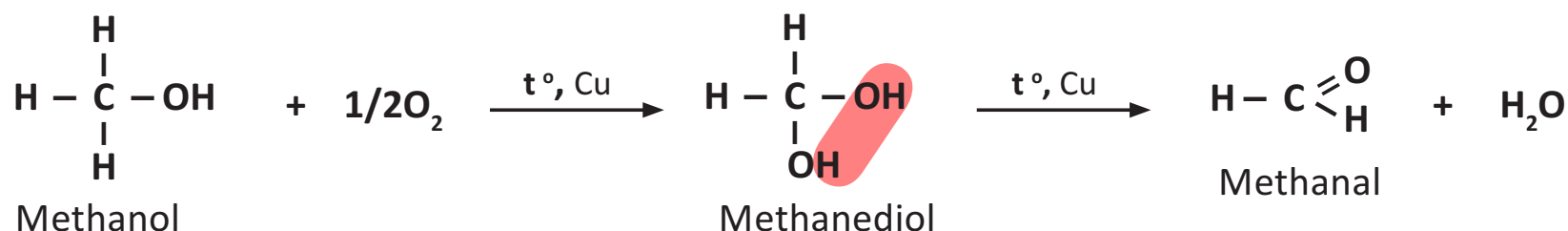
Aldehydes burn, yielding carbon dioxide and water. For example:



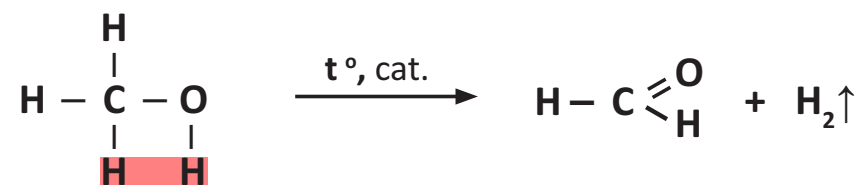


PRODUCTION

Aldehydes can be prepared from primary alcohols (the -OH group is attached to a primary C atom) with the same number of C atoms in their molecules. Alcohols are oxidized under heating and in the presence of catalysts (for example a mixture of iron oxide, molybdenum and vanadium). Dihydric alcohols are produced. They are very unstable – one water molecule is released and an aldehyde is formed (in Latin language **alcohol dehydrogenatus** means dehydrogenated alcohol). If methanol is oxidized the intermediate is methanediol:

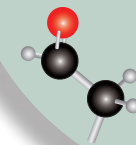


If the alcohol is heated in the presence of effective catalysts undergoes a process of dehydrogenation of the alcohol. For example methanol loses two hydrogen atoms and transforms into methanal:



Ethanal can be prepared also by hydrating ethyne (adding water to ethyne) – see chapter „Hydrocarbons“, p. 58.

On an industrial scale ethanal is produced in a process of catalytic oxidation of ethene C_2H_4 (see your Study book).



USES

Methanal (formaldehyde) is a major industrial chemical. It is mainly used in the **production of polymers**. If it polymerizes with phenol, urea $\text{H}_2\text{N}-\text{C}(=\text{O})-\text{NH}_2$, melamine $\text{H}_2\text{N}-\text{C}(=\text{N})=\text{N}-\text{C}(=\text{N})=\text{N}-\text{NH}_2$ hard resins are produced.

They are used in adhesives to make insulations and moulded products. More than the half of the produced methanal is transformed into **formaldehyde resins**. Aqueous solutions of formaldehyde are **disinfectants** as it kills many bacteria, fungi, moulds.

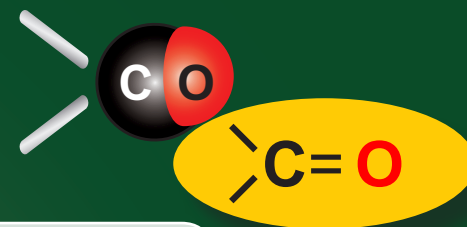
Ethanal is a start material in the preparation of organic compounds such as ethanoic (acetic) acid, its ester with ethanol and others. Ethanal is found in coffee, tea, alcohol beverages, tobacco smoke. In the organism ethanol is oxidized to ethanal by the action of a specific enzyme. Ethanal is much more toxic than ethanol and is responsible for many of the negative effects of the alcohol consumption including hangover.

CAN YOU ANSWER THESE QUESTIONS ?

1. What is a carbonyl group?
2. What are aldehydes?
3. Why are aldehydes reactive compounds?
4. Why are aldehydes prepared from primary alcohols?
5. How is the 5-carbon atoms aldehyde called?
6. At standard conditions ethanal is in liquid state while ethane is gaseous. Why?
7. How to distinguish between ethanol and ethanal?
7. Why is methanal used as disinfectant?
8. Can you enumerate three POM (polyformaldehyde) products?

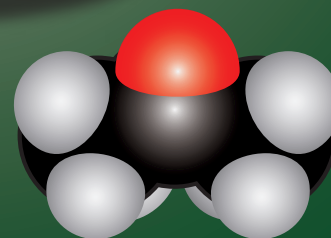
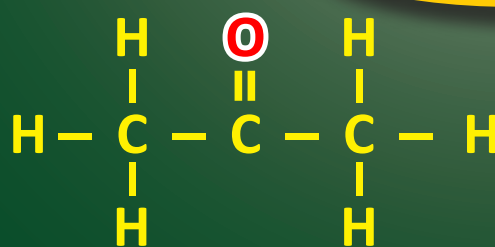
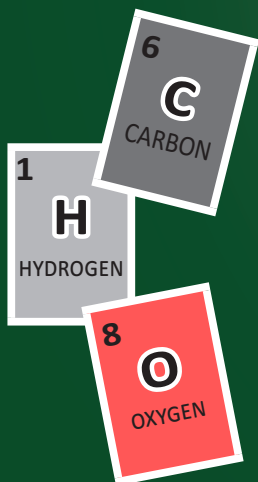
37

KETONES. PROPANONE



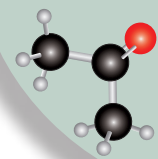
KEY TOPICS

1. What are ketones?
2. How to name ketones?
3. What is the simplest ketone?
4. Why is propanone less reactive than methanal and ethanal?
5. Why is propanone a key material for many industrial processes?



KEY WORDS

- Ketone
- Ketone group
- Propanone
- Acetone
- Dimethyl ketone

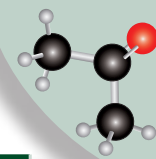


KETONES are a major class of organic compounds. They always have a carbonyl group >C=O in their molecule but unlike aldehydes it is **always „inside“ the main chain** – the carbon atom of the carbonyl group is bonded to two radicals (two, usually different, carbon chains). This functional group is called **ketone group**. For example: $\text{O}=\text{C} \begin{matrix} \text{C}_2\text{H}_5 \\ \text{CH}_3 \end{matrix}$

Ketones, like aldehydes, are considered as derivative of hydrocarbons – two hydrogen atoms bonded to the same carbon atom inside the hydrocarbon chain have been replaced by a double bonded oxygen atom:



KETONES ARE ORGANIC COMPOUNDS WITH KETONE GROUPS $\text{O}=\text{C} \begin{matrix} \text{R}_1 \\ \text{R}_2 \end{matrix}$ IN THEIR MOLECULES.



HOW TO NAME KETONES?

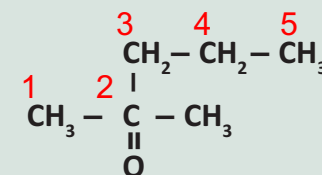
Ketones systematic names are formed following the same rules as for aldehydes, but the added suffix is „-**one**“ (the final „e“ of the alkane name is dropped): Remember that **the carbon atom of the ketone group is never an end atom**. The place of the ketone group is identified by the number of its carbon atom always starting the numbering from the nearest to the ketone group end of the carbon chain. For example:

KETONES	
CONDENSED FORMULA	NAME
$\text{H}_3\text{C} - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{CH}_3$	propan one (acetone)
$\text{H}_3\text{C} - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{CH}_2 - \text{CH}_3$	butan one
$\text{H}_3\text{C} - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$	pentan- 2-one
$\text{H}_3\text{C} - \text{CH}_2 - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{CH}_2 - \text{CH}_3$	pentan- 3-one

PROBLEM!

Name the ketone: $\text{CH}_3 - \overset{\text{C}_3\text{H}_7}{\underset{\text{O}}{\underset{\parallel}{\text{C}}}} - \text{CH}_2 - \text{CH}_3$

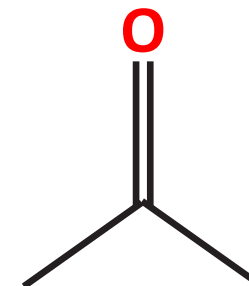
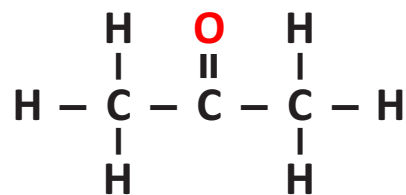
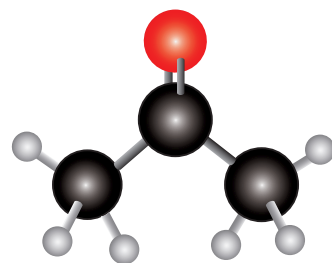
- SOLUTION:**
1. Determine the longest carbon chain that contains the ketone group and number the carbon atoms:
 2. The main chain gives the name of the ketone – this is a branched pentan-2-one.
 3. Name the branch chain: 2-methyl



ANSWER: The name of the compound is **2-methylpentan-2-one**.

Propanone, commonly known as *acetone* or *dimethyl ketone*, is the simplest ketone as the carbonyl group >C=O is bonded to two methyl groups ($-\text{CH}_3$).

PROPANONE

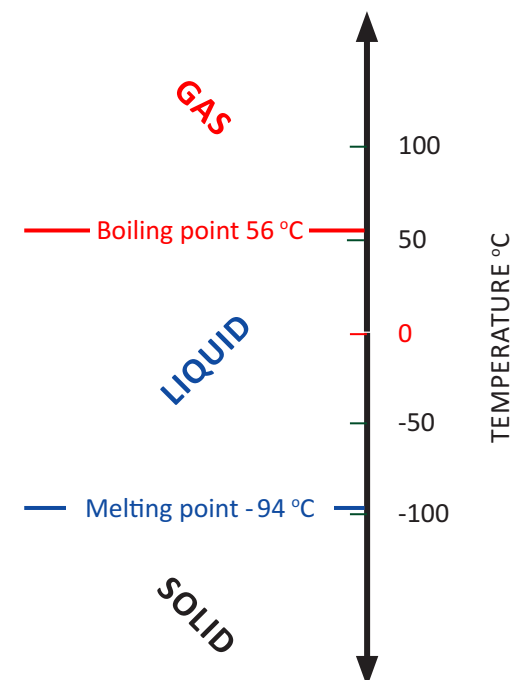


PHYSICAL PROPERTIES

Propanone is a colourless, volatile, flammable liquid with a specific sharp odour. It is lighter than water (its density is 790 kg/m^3). At standard pressure it boils at 56°C and at temperatures lower than -94°C it is solid. It is completely miscible with water. Propanone is a very good solvent of many organic compounds.

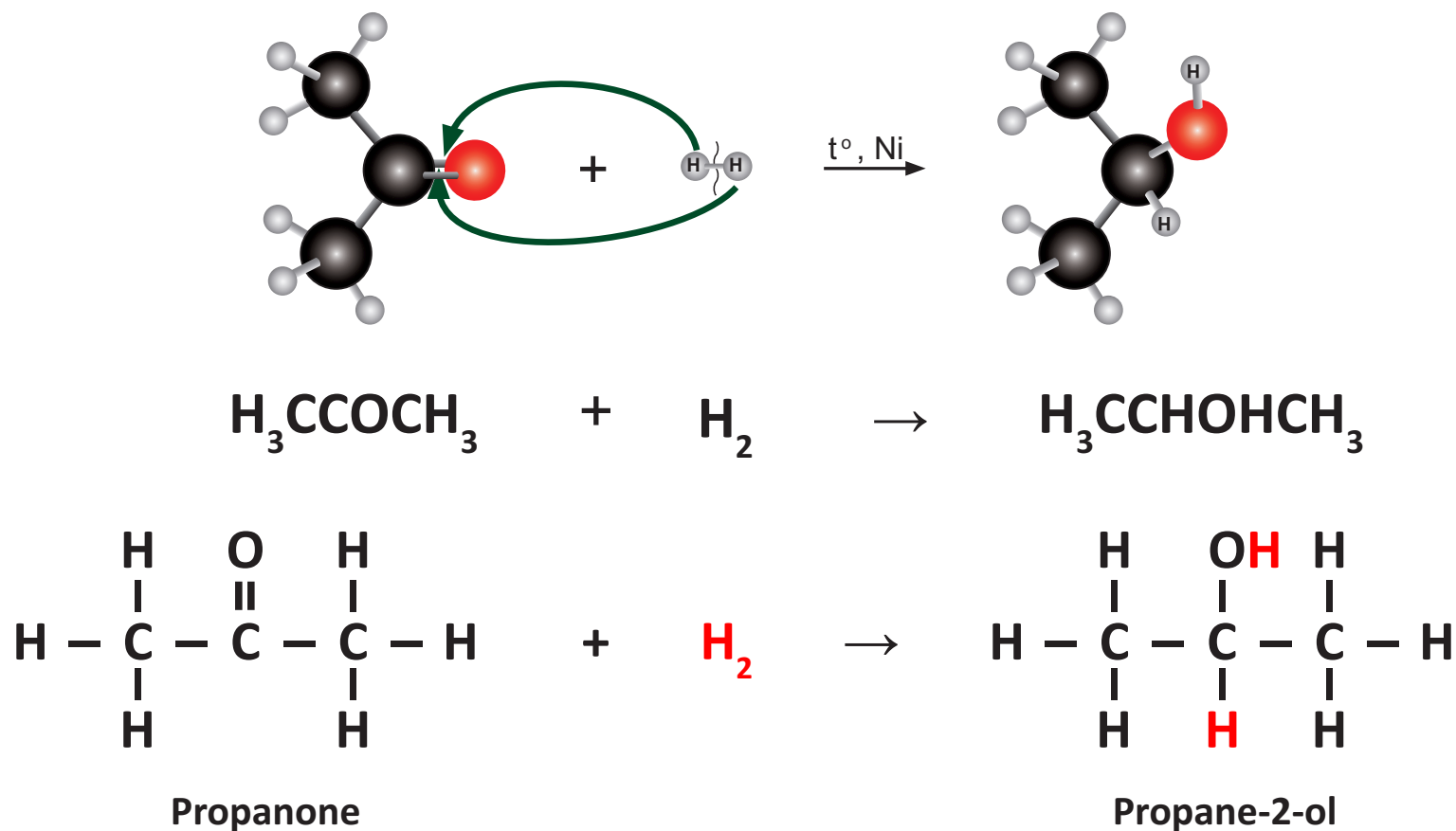
Propanone is found in small amounts in the urine and the blood. Its quantity is greater in people with diabetes.

A long exposure to concentrated propanone vapours may cause irritation of eyes and mucous and may affect the brain.

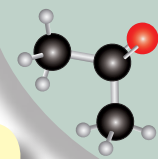


CHEMICAL PROPERTIES

Similarly to aldehydes propanone takes part in a reaction of **hydrogenation** – one of the bonds of the double C = O bond breaks down and two hydrogen atoms are added to the propanone molecule. The product is a secondary alcohol (propan-2-ol). The reaction is catalytic and undergoes under heating:



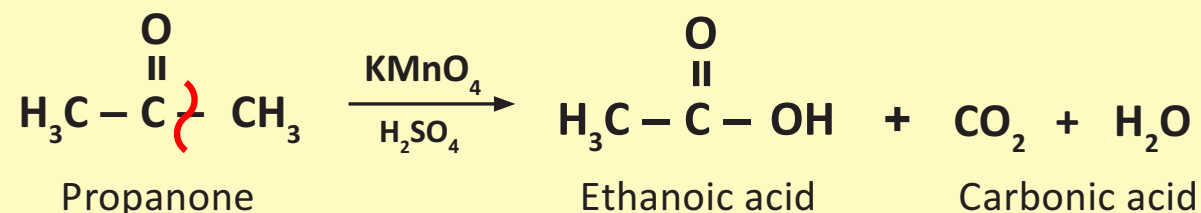
This addition reaction is much difficult than the hydrogenation of aldehydes.



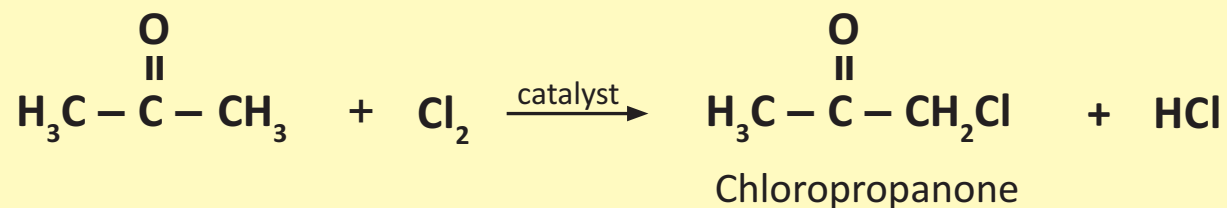
It is interesting to know:

Aldehydes and ketones display common properties owing to the functional carbonyl group in their molecules. However they exhibit some specific properties as the carbon atom of the aldehyde group is always a primary C atom while the ketone group contains always a secondary C atom.

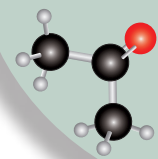
Propanone is less reactive than methanal and ethanal. It does not react with Ag_2O (ammonia solution) or freshly precipitated $\text{Cu}(\text{OH})_2$ and does not polymerize. But it discolours the purple water solution of KMnO_4 (in the presence of H_2SO_4) yielding ethanoic acid and carbonic acid – one of the C – C bonds breaks down:



Propanone can take part in reactions involving **the methyl radicals** $-\text{CH}_3$. Typical is the catalytic reaction of **halogenation** – hydrogen atom is substituted to produce halogenopropanone (or halogenoacetone). For instance:

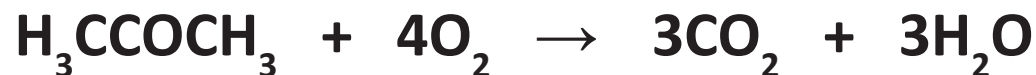


Chloropropanone and bromopropanone are lachrymatory agents.



COMBUSTION

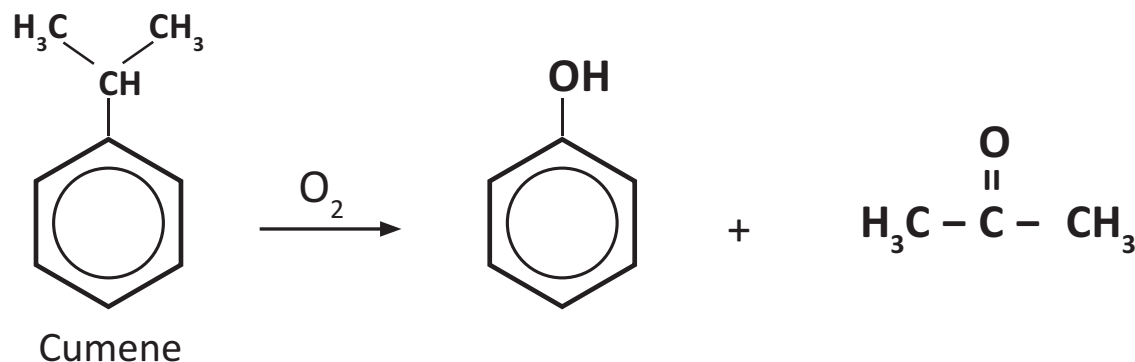
Propanone burns – the products are carbon dioxide CO₂ and water:



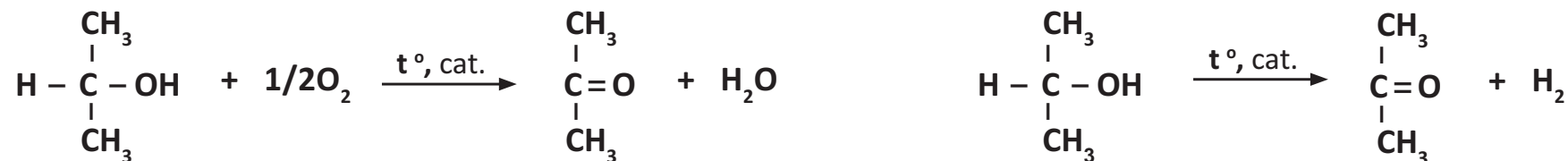
A mixtures of propanone vapours and air can explode.

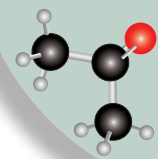
PRODUCTION

On an industrial scale propanone is mainly produced in the *cumene* process – oxidation of isopropylbenzene (cumene) to produce phenol and propanone:



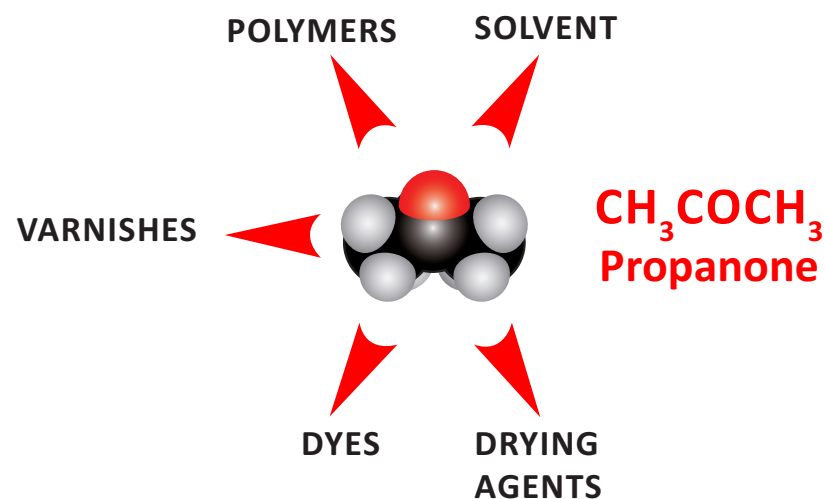
Another way is the catalytic reaction with oxygen or dehydrogenation under heating of propan-2-ol:





USES

Annually in the world are produced millions of tonnes of propanone. It is mainly used as a solvent and in the production of polymers (for example bisphenol A (see p. 32), produced from propanone and phenol, is an essential component of many plastics). As propanone is volatile (easily evaporates) and is readily miscible with water, it is used as a drying agent.



CAN YOU ANSWER THESE QUESTIONS ?

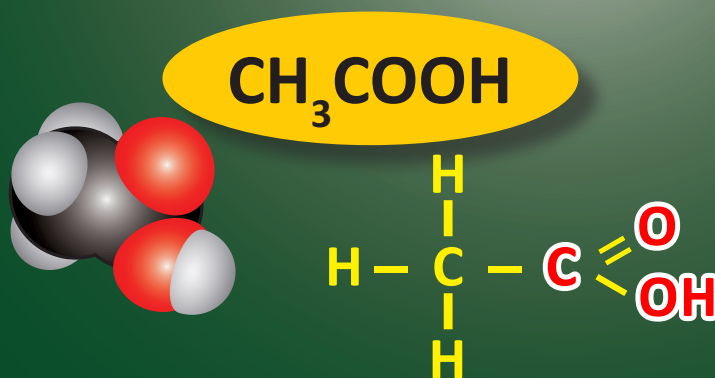
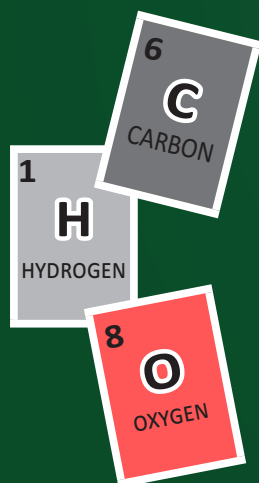
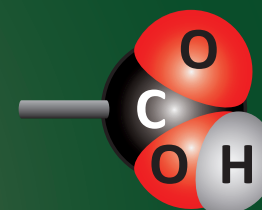
1. What is the difference between an aldehyde group and a ketone group?
2. Why is propanone the simplest ketone?
3. Why is propanone less reactive than methanal and ethanal?
4. How to distinguish between ethanol, ethanal and propanone?
5. Why must safety precautions for flammable liquids be respected when working with propanone?
6. Why is propanone used to produce dyes and varnishes?
7. Propanone is a very good solvent of many organic compounds but is not used to prepare herbal extracts. Why?

38

CARBOXYLIC ACIDS. ETHANOIC ACID

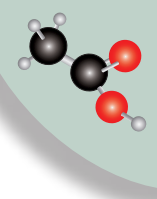
KEY TOPICS

1. What are carboxylic acids?
2. How to name carboxylic acids?
3. Why is ethanoic acid a weak acid?
4. How do organic acids react with alcohols?
5. What would happen to wine if exposed to air for a long time?



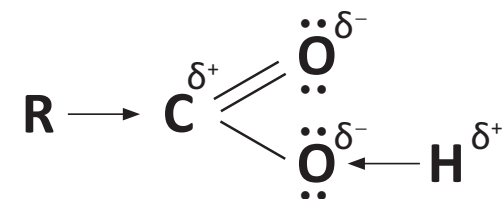
KEY WORDS

- Carboxyl group
- Carboxylic acid
- Methanoic acid (Formic acid)
- Ethanoic acid (Acetic acid)
- Glacial acetic acid
- Ethanoate ions
- Esterification
- Esters



The atomic group $-\text{C} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{OH} \end{smallmatrix}$ (a carbonyl group >C=O bonded to a hydroxy group $-\text{OH}$) is another major functional group essential to the chemical activity of organic compounds. It is called **carboxyl group**. In condensed structural formulae it is expressed as **$-\text{COOH}$** .

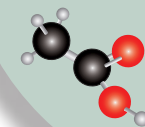
Owing to the effect of the carbonyl group the $\text{O}-\text{H}$ covalent bond of the hydroxy group is strongly polarized. In aqueous solutions the hydrogen atom is easily liberated as a positive hydrogen ion H^+ (H_3O^+). So these compounds are **organic acids**. They are called **carboxylic acids**.



$\text{R}-\text{COOH}$
Carboxylic acid

CARBOXYLIC ACIDS ARE ORGANIC COMPOUNDS WITH CARBOXYL GROUPS $-\text{C} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{OH} \end{smallmatrix}$ IN THEIR MOLECULES.

The general formula of the monovalent (with one carboxyl group) saturated carboxylic acids is **$\text{C}_n\text{H}_{2n+1}\text{COOH}$** . The simplest carboxylic acids are the methanoic acid **HCOOH** and the ethanoic acid **CH_3COOH** . Methanoic acid was first isolated from red ants and was named **formic acid** (in Latin „*formica*“ means „*ant*“). It is an antibacterial agent and a preservative.



HOW TO NAME CARBOXYLIC ACIDS?

Aliphatic acids with one -COOH group in their molecules are named (according to the IUPAC nomenclature) after the name of the aliphatic hydrocarbon with the same number of C atoms, dropping the final „e“, adding the suffix „-oic“ and the word **acid**. For instance:

methane~~X~~ $\rightarrow$ methan + oic + acid = methanoic acid **H-COOH**

ethane~~X~~ $\rightarrow$ ethan + oic + acid = ethanoic acid **H₃C-COOH**

PROBLEM!

Express the molecular formula and name the saturated monovalent carboxylic acid with three C atoms in its molecules.

SOLUTION: From the general formula of this class of organic acids it follows that $n = 2$.

So there are $2n + 1 = 5$ H atoms in the hydrocarbon chain $\text{-C}_2\text{H}_5$ and the molecular formula of this acid is $\text{C}_2\text{H}_5\text{COOH}$.

The name of the acid, according to the IUPAC recommendations, is:

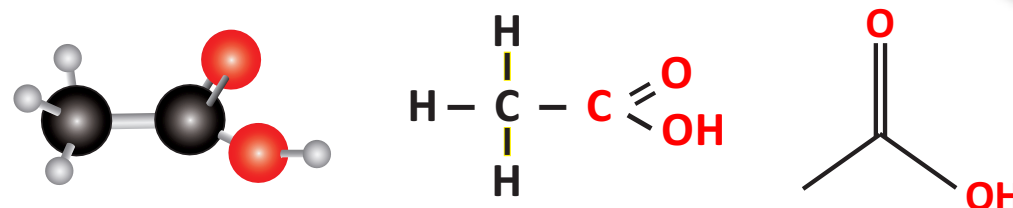
propane~~X~~ $\rightarrow$ propan + oic + acid = propanoic acid

ANSWER: The saturated aliphatic monovalent carboxylic acid with 3 C atom is **propanoic acid** $\text{C}_2\text{H}_5\text{COOH}$.

One of the most used carboxylic acid is the **ethanoic acid** commonly known as **acetic acid**.

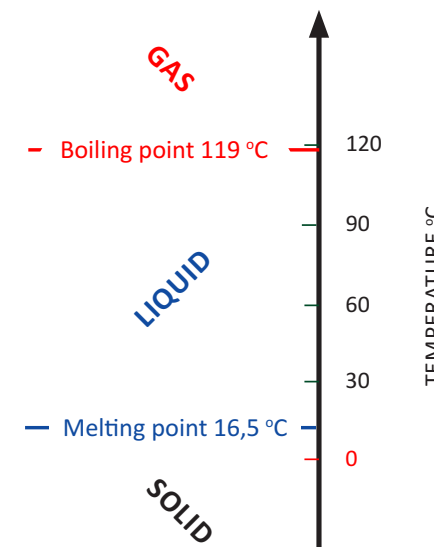
ETHANOIC ACID

Ethanoic acid is known from ancient times – since people have been producing wine. Alcoholic beverages can be oxidized by the oxygen in the air under the action of acetic acid bacteria to produce ethanoic acid. Vinegar is an aqueous solution (3 – 9 %, some times more concentrated) of ethanoic acid.



PHYSICAL PROPERTIES

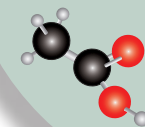
Ethanoic acid is a colourless liquid with a specific pungent smell and sour taste. It is completely miscible with water. At standard pressure it freezes at 16,5 °C, forming crystals which look like glacial crystals and is called **glacial acetic acid**. Ethanoic acid boils at a relatively high temperature (119 °C) because of the strong interactions between its molecules – more energy (compared to ethanol) is needed to overcome the electrostatic attraction between molecules as the O–H bond in the carboxyl group is much polar.



Owing to the strong polarization of the O–H bond, ethanoic acid dissociates in water, yielding a negative **ethanoate** (acetate) ion CH₃COO[−] and a positive hydrogen ion H⁺ (H₃O⁺):



Because of the presence of hydrogen ions H⁺ the blue litmus turns red in aqueous solutions of ethanoic acid. But not all molecules dissociate in water and acetic acid is considered as a weak acid.



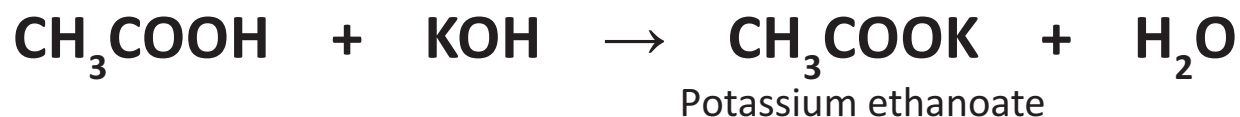
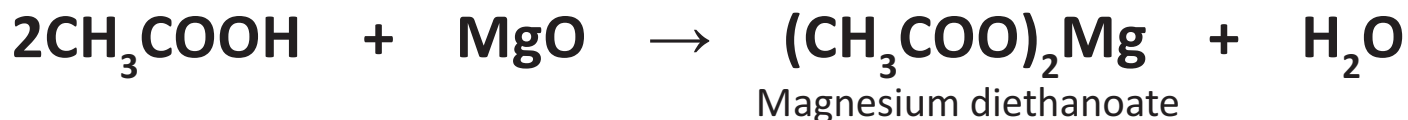
CHEMICAL PROPERTIES

Ethanoic acid displays the common for all acids chemical properties – it reacts with **active metals**, **basic oxides and bases**.

In the reactions with active metals hydrogen is liberated and salts are produced:

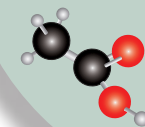


In the reactions with basic oxides and bases the products are salts and water:



This is a reaction of neutralization and the temperature raises as heat is evolved.

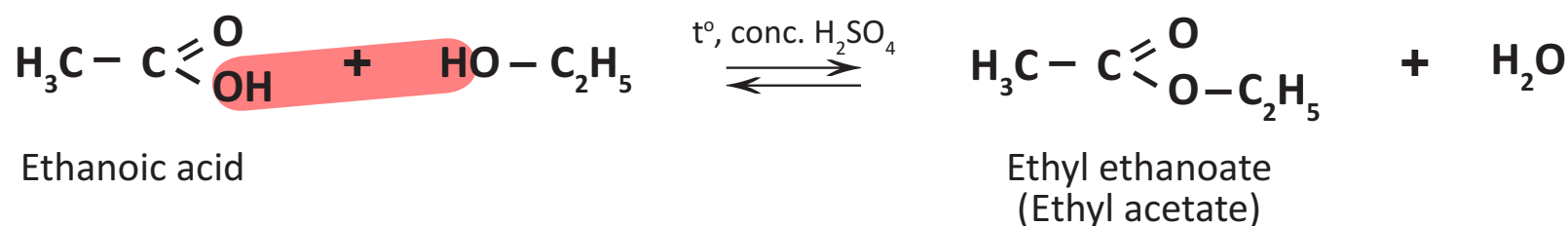
The reactions are slow compared to the reactions of the inorganic acids (for example HCl, H₂SO₄, HNO₃).



Carboxylic acids are oxygen-containing acids and similarly to HNO_3 they react with alcohols (see p. 17). The products are an ester and water. The reaction is molecular, reversible and slow and is called a reaction of **esterification**:



For example ethanoic acid reacts with ethanol to produce ethyl ethanoate (ethyl ester of ethanoic acid) and water. The esterification reaction undergoes in the presence of a catalyst* (conc. H_2SO_4):

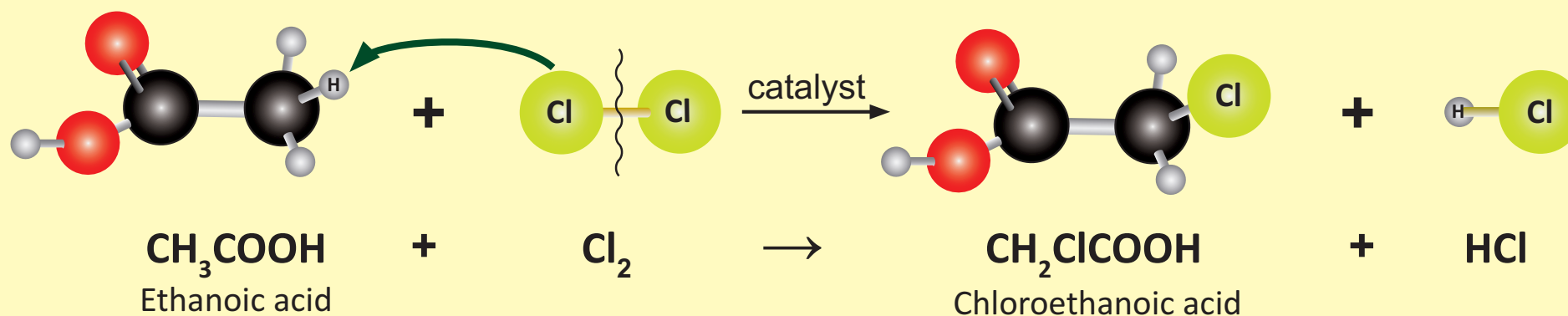


The ester (ethyl ethanoate) is a colourless liquid with a fruity odour and is used as an artificial food flavour and as a solvent.

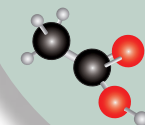
* **Catalysts** are substances that accelerate chemical reactions without themselves being consumed.

It is interesting to know:

Ethanoic acid reacts with halogens. Hydrogen atoms in the methyl group -CH_3 are substituted by halogen atoms. For instance in the reaction of chlorination the product is chloroethanoic acid (commonly known as chloroacetic acid):



Chloroethanoic acid is more reactive than ethanoic acid. If there is enough chlorine all three hydrogen atoms of the methyl group are substituted by chlorine atoms.



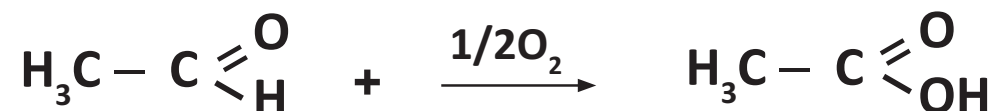
PRODUCTION

The oxidation of ethanol by the oxygen in the air under the action of specific bacteria is a well known biochemical process. The products are ethanoic acid and water:



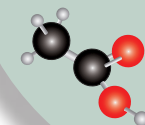
That would happen if wine has been exposed to air for a long time.

The oxidation of ethanal is a common reaction, yielding ethanoic acid:



On an industrial scale ethanoic acid is produced in a reaction of methanol with carbon monoxide (process of catalytic carbonylation of methanol):

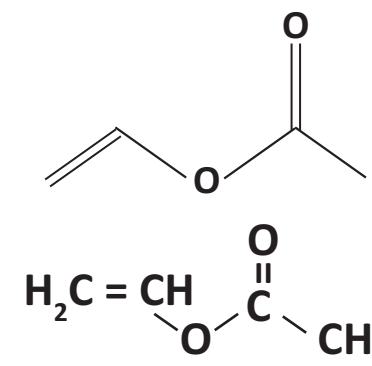




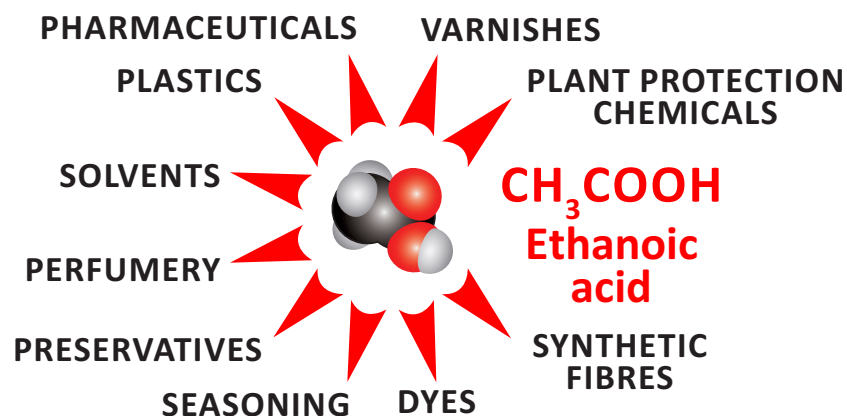
USES

Vinegar (dilute water solutions of ethanoic acid) is a seasoning and a preservative. But it is also a cleaner (for example to remove spots of wet cups from the wood furniture, carpet stains, etc.). The mixture of vinegar and baking soda can be effective to unclog drains.

In the industry ethanoic acid is a start material for the production of ethenyl ethanoate (vinyl acetate) used in the production of plastics, resins, textile, etc. and also cellulose acetate – a key material for the production of synthetic fibres and plastics.



Ethenyl ethanoate
(vinyl acetate)



Ethanoic acid is also an intermediate for the production of dyes, pharmaceuticals, plant protection chemicals, varnishes. The odour of some esters of the ethanoic acid is very pleasant and they are used to prepare perfume compositions. Ethyl ethanoate is a good solvent of varnishes.

CAN YOU ANSWER THESE QUESTIONS ?

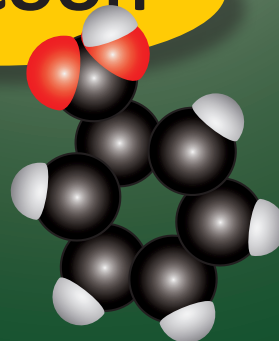
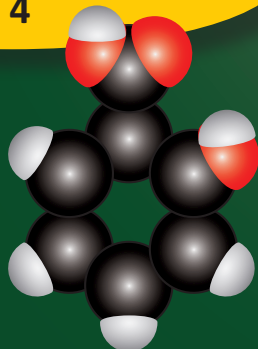
1. Why are organic compounds with carboxyl groups in their molecules acids?
2. Carboxylic acids are stronger acid than phenol. Why?
3. Why does ethanoic acid boil at a relatively high temperature?
4. Methanoic acid HCOOH reacts with Ag_2O (silver mirror test), while ethanoic acid does not react. Why?
5. How to produce ethanoic acid?
6. Is it good to leave an open bottle of wine?
7. Why is a mixture of vinegar and baking soda used to unclog drains?
8. What is ethanoic acid used for in everyday life?

39

BENZOIC ACID. 2-HYDROXYBENZOIC ACID

KEY TOPICS

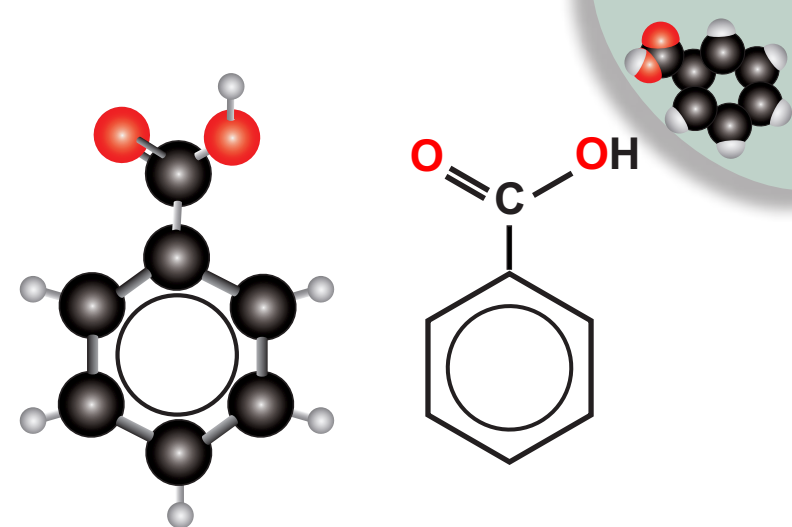
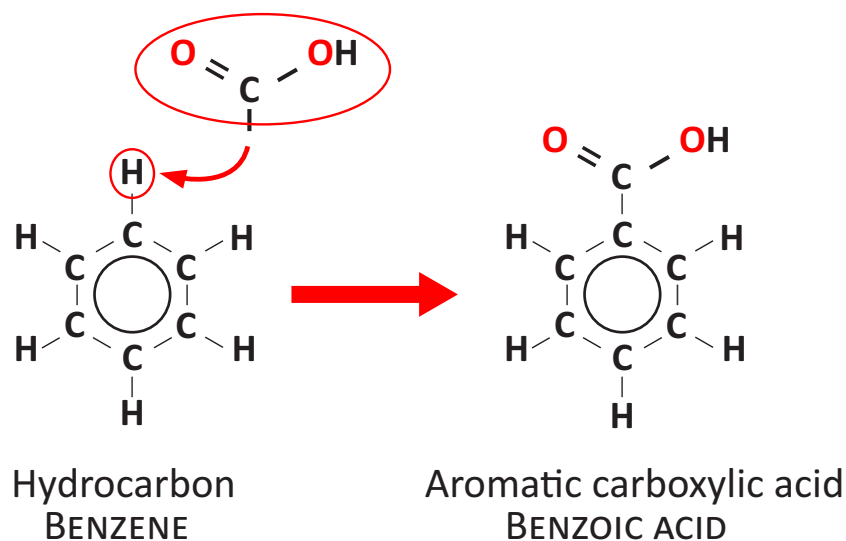
1. What is the simplest aromatic carboxylic acid?
2. What is E210, E211?
3. What is 2-hydroxybenzoic acid used for?
4. What is aspirin?



KEY WORDS

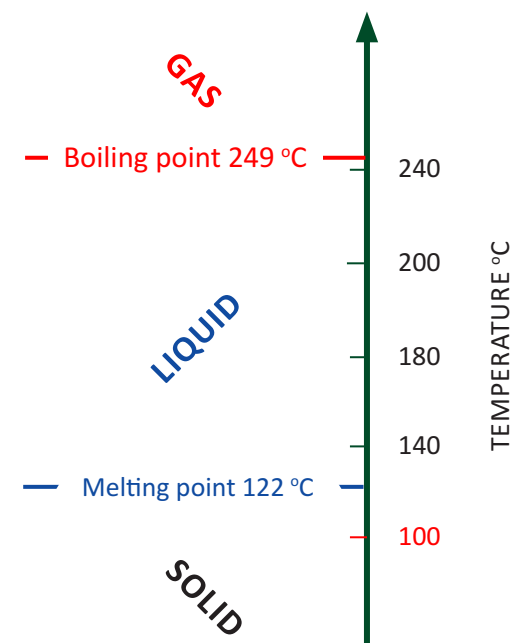
- Benzoic acid
- Benzoate ion
- 2-hydroxybenzoic acid
- Salicylic acid
- Acetylsalicylic acid
- Aspirin
- Phenylsalicylic acid
- Salol

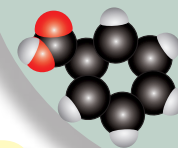
BENZOIC ACID C_6H_5COOH is the simplest aromatic carboxylic acid. In its molecules one carboxyl group is directly bonded to an aromatic ring thus substituting one H atom if compared to the benzene molecule. The name „benzoic“ originates from „gum benzoin“ – a natural gum from which it has been extracted.



PHYSICAL PROPERTIES

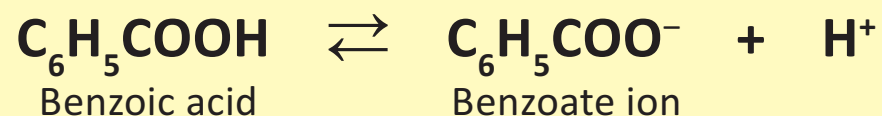
Benzoic acid is a crystalline colourless substance with a peculiar smell. It is heavier than water (its density is 1.279 kg/m^3). Under strong heating it sublimates. It melts at 122°C and boils at 249°C . Benzoic acid is slightly soluble in water but its solubility increases if the temperature rises. It is soluble in many organic solvents (methanol, ethanol, propanol, propanone, benzene, tetrachloromethane, etc.).





It is interesting to know:

As all weak acids benzoic acid dissociates partially in water, yielding negative **benzoate** ions and positive hydrogen ions:



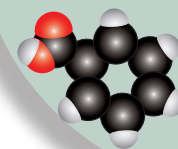
In aqueous solutions of benzoic acid the blue litmus turns red.

CHEMICAL PROPERTIES

Both the functional carboxyl group -COOH and the aromatic ring might be involved in chemical interactions.

REACTIONS OF THE -COOH GROUP

These reactions undergo easy as compared to the saturated carboxylic acids (like ethanoic acid for example) as the O-H bond is more polarized. All reactions for the ethanoic acid are possible – with active metals, basic oxides, bases, salts of weak acids and esterification.



PROBLEM!

How many moles of hydrogen H_2 are evolved in the reaction of 4 moles of benzoic acid with sodium Na?

SOLUTION: The chemical equation of the reaction is:

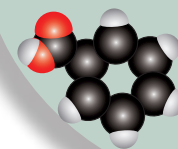


The incomplete molar ratio for benzoic acid and hydrogen is:

$$n(\text{C}_6\text{H}_5\text{COOH}) : n(\text{H}_2) = 2 : 1.$$

$$\text{So } n(\text{H}_2) = (1/2)n(\text{C}_6\text{H}_5\text{COOH}) = (1/2) \cdot 4 = 2 \text{ moles}$$

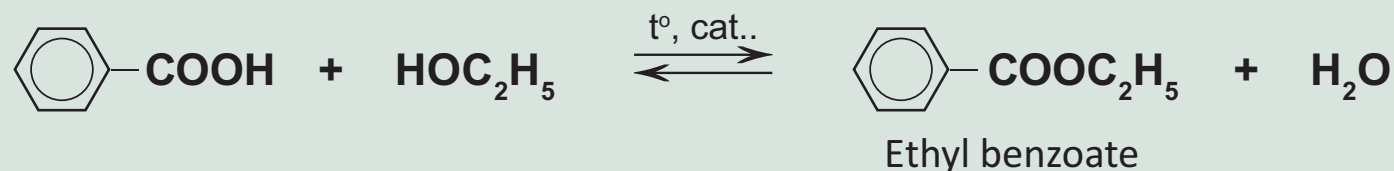
ANSWER: In the reaction of 4 moles of benzoic acid with sodium **2 moles** of H_2 are evolved.



PROBLEM!

How many moles of benzoic acid do react with ethanol to produce 10 moles of water? What type of reaction is that?

SOLUTION: The chemical equation of the reaction is:

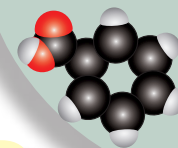


The incomplete molar ratio for benzoic acid and water is:

$$n(\text{C}_6\text{H}_5\text{COOH}) : n(\text{H}_2\text{O}) = 1 : 1.$$

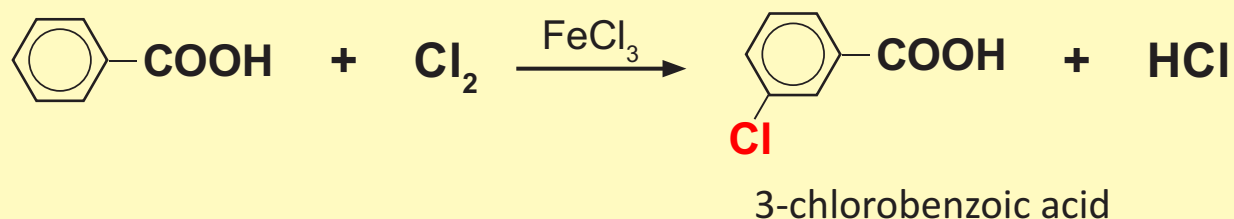
$$\text{So } n(\text{H}_2\text{O}) = n(\text{C}_6\text{H}_5\text{COOH}) = 10 \text{ moles}$$

ANSWER: To produce 10 moles of water, **10 moles** of benzoic acid have to react with ethanol. This is a reaction of **ESTERIFICATION**.

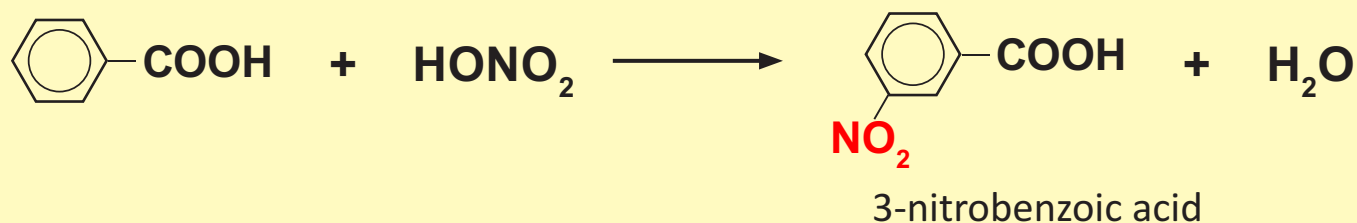


CHEMICAL REACTIONS OF THE AROMATIC RING

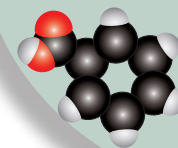
Substitution reactions of the aromatic ring can take place but the carboxyl group deters the substitution of the H atoms. So these reactions are slow compared to the substitution reactions of benzene. The substituents are first directed to the 3rd (or *meta*) C atom relative to the carbon atom bonded to the -COOH group. Typical reactions are the *chlorination* and the *nitration* of benzoic acid:



3-chlorobenzoic acid is a start material of many organic synthesis.

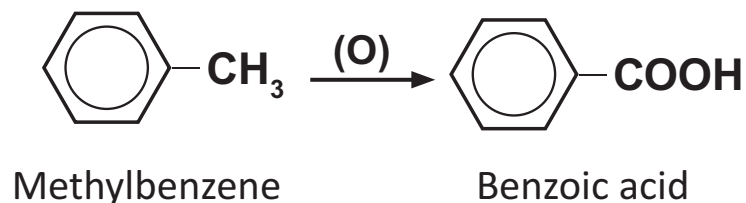


3-nitrobenzoic acid is stronger than benzoic acid.



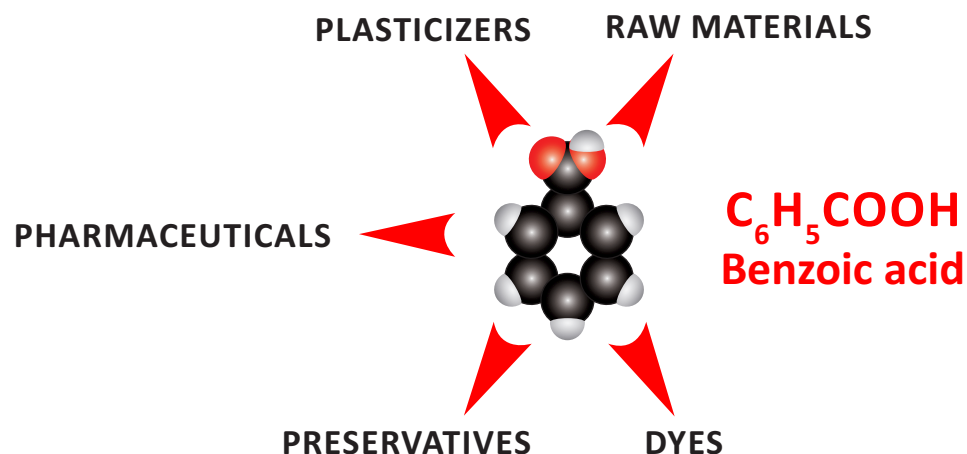
PRODUCTION

In the industry benzoic acid is produced in a catalytic process of oxidation of methylbenzene:



USES

Benzoic acid is used in many organic synthesis. Some of its salts and esters are active components of ointments. They are also used as components (plasticizers) of some plastics. Benzoic acid and its sodium salt are used as food preservatives. E210 (benzoic acid), E211 (sodium benzoate), E212 (potassium benzoate), E213 (calcium benzoate), E214 – E219 (derivatives of the benzoic acid) are food additives, permitted in the EU, used as antibacterial and antifungal food preservatives.

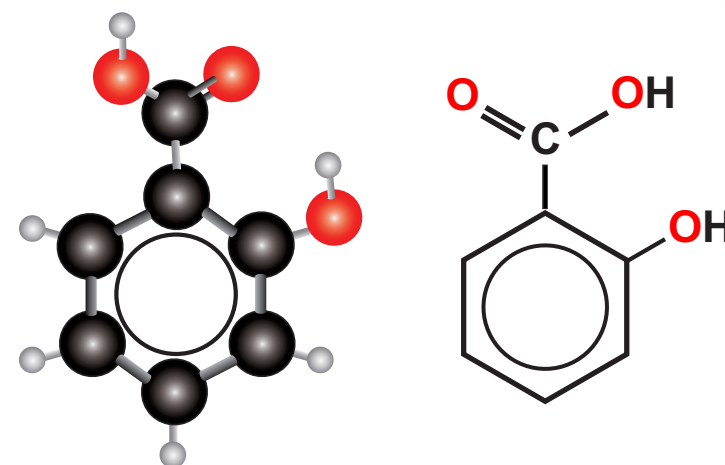
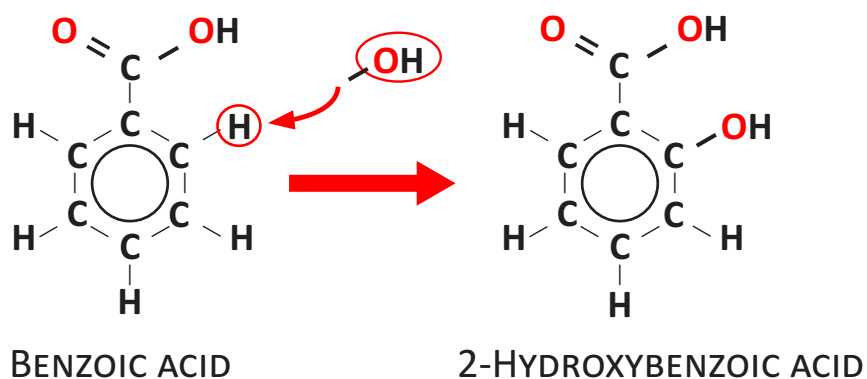


PHYSIOLOGICAL ACTION

The concentration of benzoic acid and sodium benzoate in plants and foods is low and these compounds are not harmful for man. But if swallowed benzoic acid can cause serious damages to organs. Prolonged or repeated exposures to benzoic acid vapours can cause skin irritation, serious eye damage and can damage organs too.

2-HYDROXYBENZOIC ACID

The molecule of 2-hydroxybenzoic acid contains two functional groups – a carboxyl group -COOH and a hydroxy group -OH . They are bonded to two adjacent C atoms of the aromatic ring, i.e. this is benzoic acid with one hydroxy group on *o*-position (*o*-hydroxybenzoic acid).

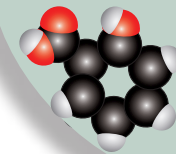


The common name of this organic acid is **salicylic acid** (the acid was first isolated from the bark of a white willow – *Salix alba*).

2-hydroxybenzoic acid is a colourless and odourless crystal solid. It is soluble in hot water. Under moderate heating it sublimates. It dissolves to different extents in many organic solvents – tetrachloromethane, benzene, methanol, ethanol, propanol, propanone, methylbenzene, etc.

2-hydroxybenzoic acid is an antiseptic and an antibacterial agent. It is also used as a preservative.

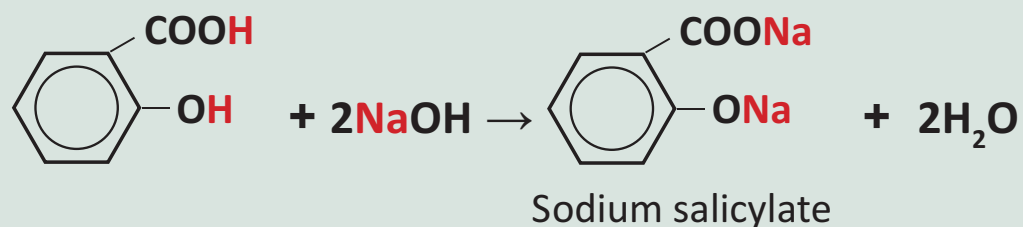
2-hydroxybenzoic acid is stronger than benzoic acid. As all acids it reacts with active metals, basic oxides, bases and salts of weak acids, yielding salts – *salicylates*.



PROBLEM!

How many moles of sodium hydroxide NaOH are needed to neutralize 5 moles of 2-hydroxybenzoic acid?

SOLUTION: Both functional groups are involved in this interaction:

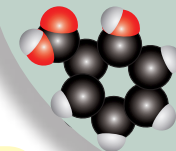


The incomplete molar ratio for 2-hydroxybenzoic acid and sodium hydroxide is:

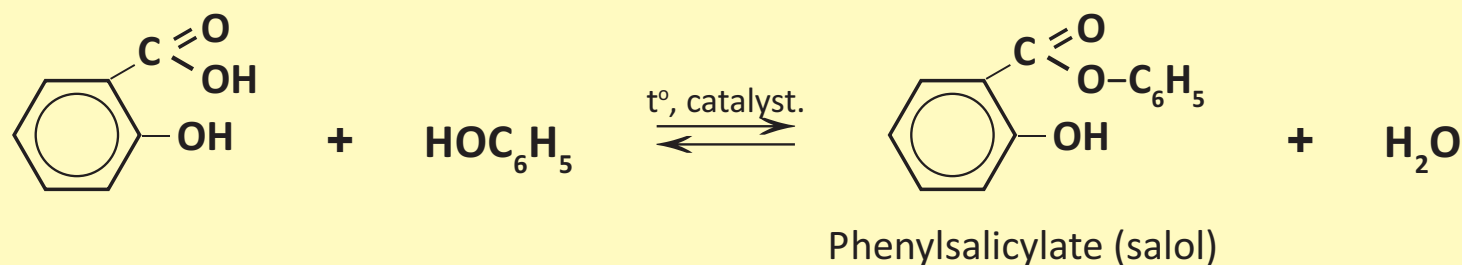
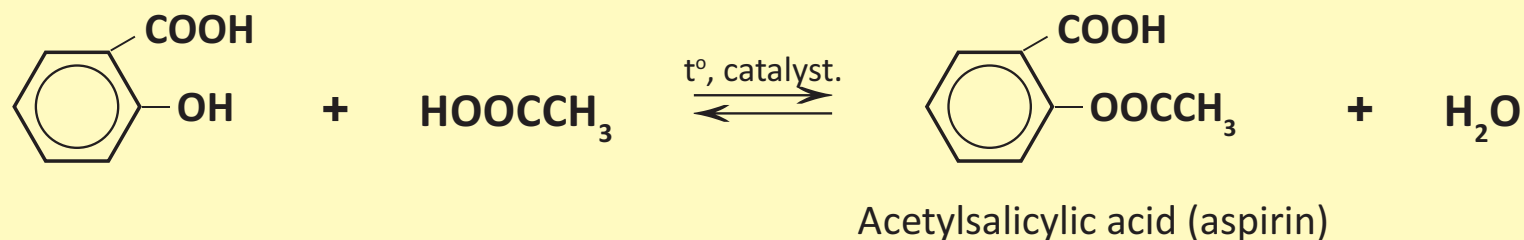
$$n(\text{HO}-\text{C}_6\text{H}_4-\text{COOH}) : n(\text{NaOH}) = 1 : 2.$$

$$\text{So } n(\text{NaOH}) = 2n(\text{HO}-\text{C}_6\text{H}_4-\text{COOH}) = 2.5 = 10 \text{ moles}$$

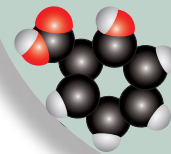
ANSWER: 10 moles of **NaOH** are required to neutralize 5 moles of $\text{HO}-\text{C}_6\text{H}_4-\text{COOH}$.



Owing to the presence of two different functional groups 2-hydroxybenzoic acid can react with acids as well as with alcohols and phenols. Both are reactions of esterification. The esters with ethanoic acid and phenol are commonly known as **aspirin** and **salol**:



Both esters are drugs. Aspirin is a widely used anti-inflammatory, analgesic (relieves pains) and antipyretic (reduces fever) drug. It is also used to prevent blood clot formation and thus prevents heart attacks and strokes. Salol is an antiseptic. 2-hydroxybenzoic acid itself is also an antiseptic with strong bactericidal action and is used as a food preservative.



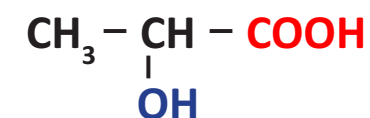
Other well known carboxylic acids with two functional groups in their molecules are the **ethandioic acid**, better known as **oxalic acid**, and **2-hydroxypropanoic acid** known as **lactic (milk) acid**.

Oxalic acid $(\text{COOH})_2$ removes rust spots. The calcium salt of oxalic acid is insoluble in water. If the content of calcium oxalates in the urine is high, kidney stones of calcium oxalate can form.



Oxalic acid

Lactic acid $\text{CH}_3\text{OHCHCOOH}$ is a product of the lactic acid fermentation of glucose or other saccharides (for example lactose) by the action of some microorganisms (for example *Lactobacillus bulgaricus* used in the yogurt production). During physical training lactic acid is accumulated in the muscles.



Lactic acid

CAN YOU ANSWER THESE QUESTIONS ?

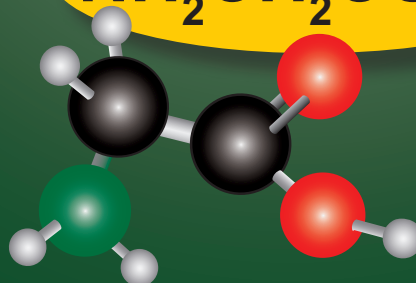
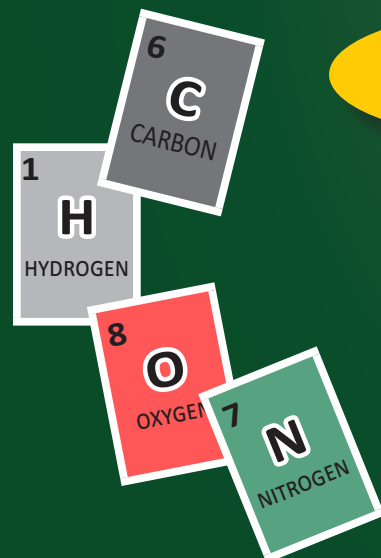
1. Why is the compound $\text{C}_6\text{H}_5\text{COOH}$ an acid?
2. Under standard conditions benzene is a volatile liquid while benzoic acid is a crystalline substance. Why?
3. Benzoic acid can be harmful for man but in spite of that it and some of its salts are used as food preservatives. Why?
4. Is 2-hydroxybenzoic acid stronger than benzoic acid? Why?
5. How to distinguish between benzoic and salicylic acid?
6. Why does 2-hydroxybenzoic acid take part in esterification reactions both with carboxylic acids and alcohols?
7. What is the product of the esterification of 2-hydroxybenzoic acid and ethanoic acid? What is its common name and what it is used for?
8. Why is aspirin used as a food preservative?

40

AMINES. AMINO ACIDS

KEY TOPICS

1. What are amines and amino acids?
2. What are α -amino acids?
3. What is the simplest amine and the simplest amino acid?
4. What is a peptide bond? Why is it important for all living organisms?



KEY WORDS

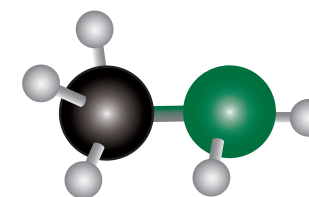
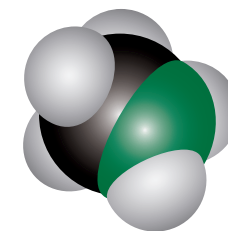
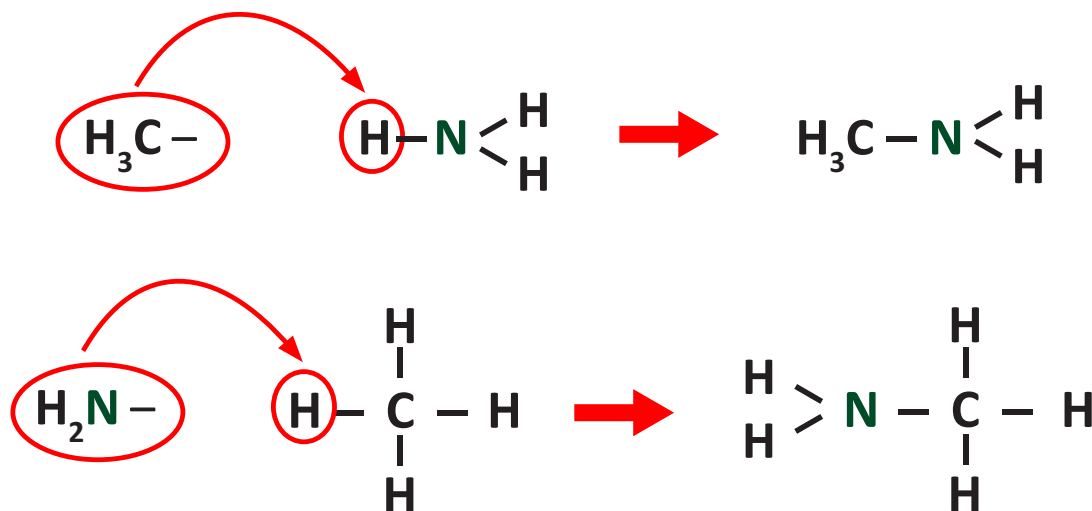
- Amines
- Methylamine
- Aminobenzene (Phenylamine, Aniline)
- Amino acid
- α -amino acid
- Peptide bond
- Polypeptide

Amines and amino acids are nitrogen containing organic compounds. Amines are the simplest nitrogen-containing organic compounds and amino acids play an important biological role.

AMINES

Amines are organic compounds composed of carbon (as all organic compounds), hydrogen and nitrogen. In organic compounds nitrogen is mainly trivalent and forms polar covalent bonds.

The simplest amine is **metylamine** CH_3NH_2 . It is considered as derived from ammonia (for this reason these organic compounds are named amines) by substituting one H atom with a methyl group $-\text{CH}_3$. But in the same time it can be a derivative of methane in whose molecules one H atom has been replaced by an amino group $-\text{NH}_2$. Both are correct:

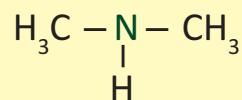


Methylamine
or Aminomethane

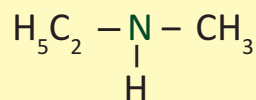
It is interesting to know:

Generally, one, two or all three atoms in the ammonia molecule can be substituted by hydrocarbon groups ($-\text{C}_2\text{H}_5$, $-\text{C}_3\text{H}_7$, $-\text{C}_4\text{H}_9$, etc.) They are named *amines* and the name of the radicals are added as prefixes. For example $\text{C}_2\text{H}_5\text{NH}_2$ – *ethylamine*; $\text{C}_6\text{H}_5\text{NH}_2$ – *phenylamine* (the simplest aromatic amine, commonly known as aniline).

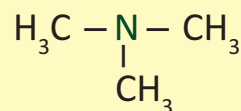
Similarly to hydrocarbons amines are **primary** (one H atom in the NH_3 molecule has been substituted by a hydrocarbon group), **secondary** (two H atoms have been substituted by hydrocarbon groups) and **tertiary** (all three H atoms have been substituted by hydrocarbon groups):



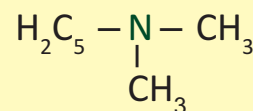
Dimethylamine



Ethylmethylaniline



Trimethylamine

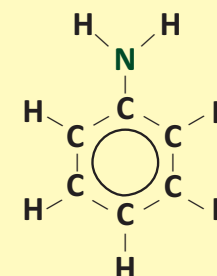
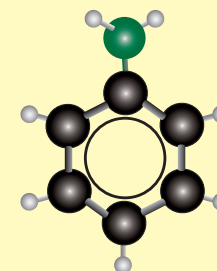
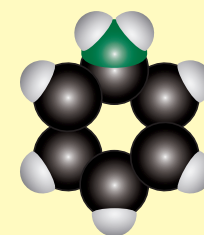


Ethylmethylaniline

Some times it is more convenient to name an amine using the name of the hydrocarbon with the same carbon chain, adding the prefix „**amino**-“. For

example phenylamine $\text{C}_6\text{H}_5\text{NH}_2$ is also named *aminobenzene*, $\begin{array}{c} \text{H}_3\text{C} - \text{CH} - \text{CH} - \text{CH}_3 \\ | \quad \quad | \\ \text{NH}_2 \quad \text{NH}_2 \end{array}$

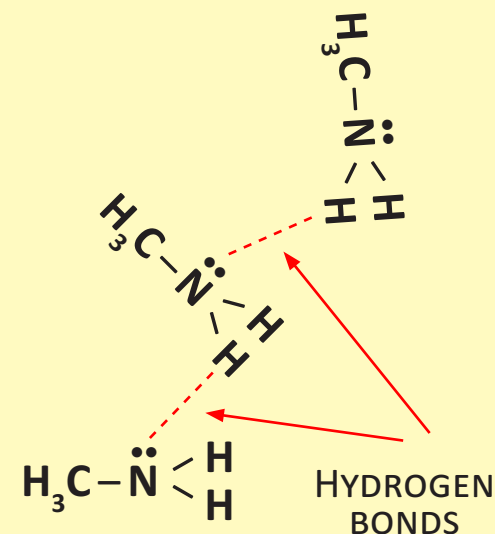
is named 2,3- diaminobutane, etc.



Phenylamine
(Aniline)

PHYSICAL PROPERTIES

The nitrogen atom of the amino group has a lone electron pair ($-\ddot{\text{N}}\text{H}_2$). It attracts the hydrogen atom of the amino group of another molecule, thus forming an intermolecular bond (called hydrogen bond). It is weak as compared to the hydrogen bonds between alcohol molecules because the nitrogen atom is less electronegative than the oxygen atom. As consequence, the melting and boiling points of the saturated amines are higher than that of alkanes, but are low if compared to the saturated alcohols with the same molecular mass.



ALKANES

AMINES

ALCOHOLS

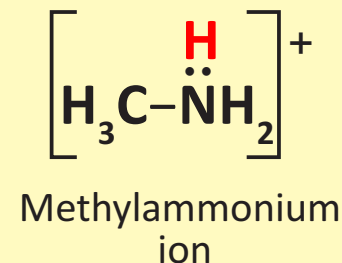
Melting and boiling points increase



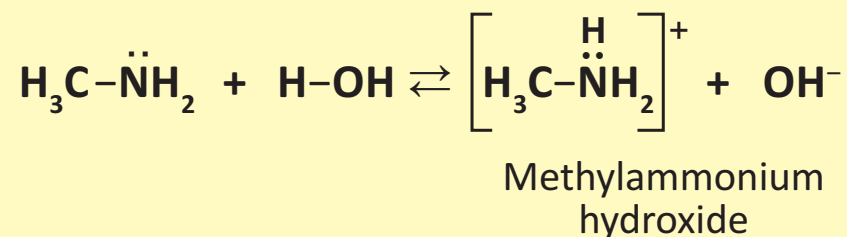
Methylamine CH_3NH_2 is a gas at STP. The other low molecular weight primary amines are liquids, while the high molecular weight amines are solid substances. Aminobenzene is a very slightly soluble in water, oily, flammable liquid with an unpleasant odour.

CHEMICAL PROPERTIES

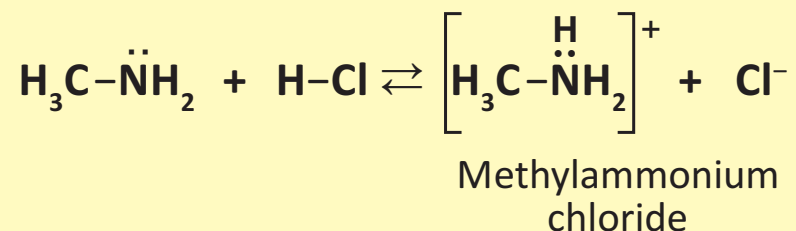
The soluble in water amines form positively charged ions in their aqueous solutions as hydrogen ions are attached to the lone electron pair of the nitrogen atom.

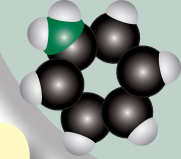


Similarly to ammonium hydroxide (NH_4OH), in aqueous solutions of methylamine CH_3NH_2 methylammonium hydroxide $\text{CH}_3\text{NH}_3\text{OH}$ is formed:

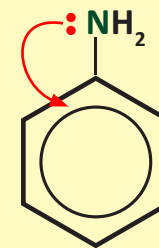


Dissolved in water amines react as bases (generally, they are stronger than ammonium hydroxide). In reactions with soluble inorganic acids soluble salts are formed:

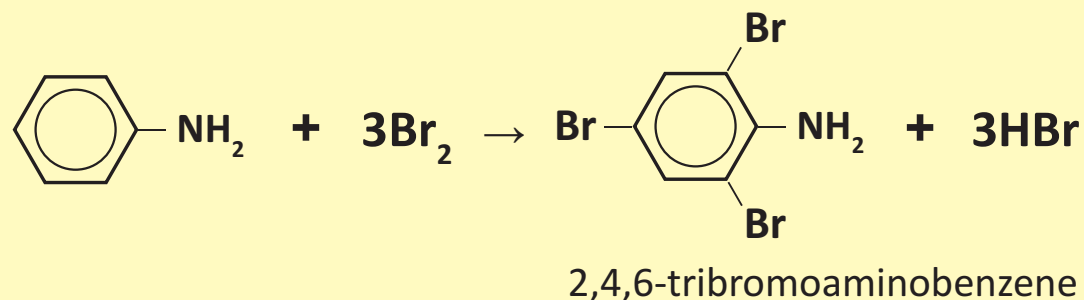




AMINO BENZENE (phenylamine or aniline) is a weak base – weaker than saturated amines and ammonia. The lone electron pair of the nitrogen atom is attracted by the 6 delocalized electrons of the aromatic ring. The lone pair is not anymore „lone“ and the partial negative charge of the nitrogen atom is lower. Thus it is more difficult for a hydrogen ion to bond to the nitrogen atom. But the substitution reactions for the aromatic ring are facilitated. For example bromine water discolours if aminobenzene is added to the solution. The -NH_2 group directs the substituents to *o*- and *p*-positions. A white precipitate of 2,4,6-tribromoaminobenzene forms:



Aminobenzene



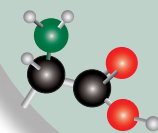
The discoloration of bromine water is a test reaction for double or triple carbon – carbon bonds. But in a substitution reaction aminobenzene also discolours bromine water (similarly to phenol).



**A COMMON TEST REACTION FOR AMINO BENZENE IS ITS
INTERACTION WITH CHLORINATED LIME – THE SOLUTION TURNS VIOLET.**

AMINO BENZENE IS A STRONG POISON.

Many amines are basic components (chemical building blocks) for organic synthesis. They are used in the production of drugs, dyes, explosives, synthetic (polyamide) fibres, corrosion inhibitors, etc.

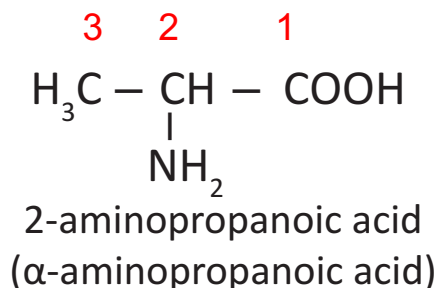
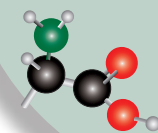


AMINO ACIDS

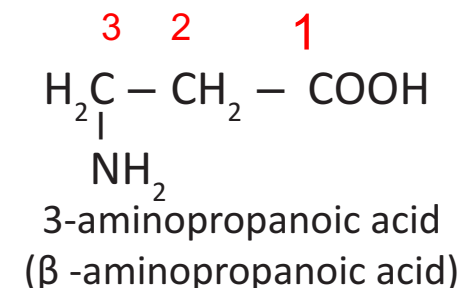
Amino acids may be considered as derived from carboxylic acids in whose molecules one or more H atoms have been substituted by amino groups. They are named simply by adding the prefix „-**amino**“ to the name of the carboxylic acid (see the table). The place of the -NH_2 group is indicated by the number of the C-atom to which it is attached. **As a rule to the C atom of the -COOH is assigned number 1.** Many amino acids (especially the biologically important) are known also by their common names.

AMINO ACIDS	
CONDENSED FORMULA	NAME
$\begin{array}{c} \text{H}_2\text{C} - \text{COOH} \\ \\ \text{NH}_2 \end{array}$	Aminoethanoic acid (Glycine)
$\begin{array}{c} \text{H}_3\text{C} - \text{CH} - \text{COOH} \\ \\ \text{NH}_2 \end{array}$	2-aminopropanoic acid (Alanine)
$\begin{array}{c} \text{H}_3\text{C} \\ \\ \text{HC} - \text{CH} - \text{COOH} \\ \quad \\ \text{H}_3\text{C} \quad \text{NH}_2 \end{array}$	2-amino-3-methylbutanoic acid (Valine)
$\text{C}_6\text{H}_5 - \text{CH}_2 - \text{CH} - \text{COOH}$ $\quad \quad $ $\quad \quad \text{NH}_2$	2-amino-3-phenylpropanoic acid (Phenylalanine)

AMINO ACIDS ARE ORGANIC COMPOUNDS WITH TWO FUNCTIONAL GROUPS IN THEIR MOLECULES – A CARBOXYL GROUP **-COOH** AND AN AMINO GROUP **-NH_2** .



If the -NH_2 group is neighbour to the -COOH group the amino acids are designated as **α -amino acids** (all acids listed in the table). If the -NH_2 group is bonded to the third C atom the acids are **β -amino acids**. If the amino group is bonded to the fourth C atom – **γ -amino acids**, etc. For living organisms the most important are the α -amino acids as they are building blocks of proteins.

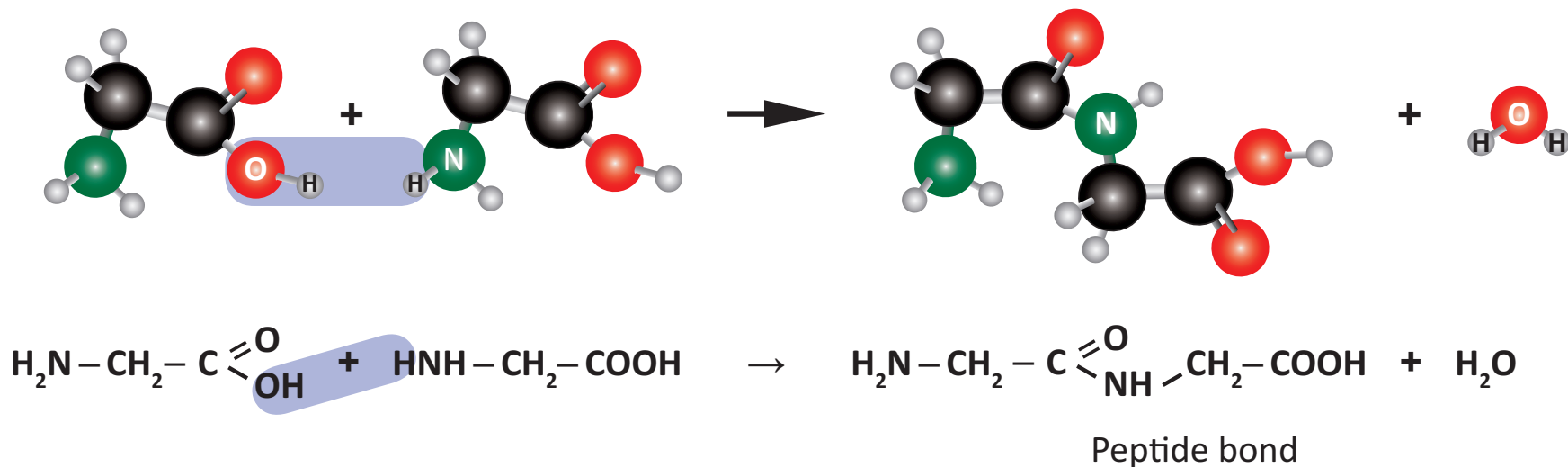


PHYSICAL PROPERTIES

Amino acids are colourless crystalline solids. They melt at relatively high temperatures (above 230°C). They are soluble in water but are insoluble in nonpolar solvents (for example benzene and other hydrocarbons).

CHEMICAL PROPERTIES OF α -AMINO ACIDS

α -amino acids react with acids (the $-\text{NH}_2$ group is involved) as well as with bases (the $-\text{COOH}$ group is involved). But for the living world the most important chemical property of α -amino acids is the ability of their molecules to bond to each other, thus forming long chains. It is not obligatory to link identical molecules. One H atom of the amino group of one molecule and the $-\text{OH}$ group of the carboxyl group of another molecule form a water molecule. The two molecules residues link to each other by the so called **peptide bond**, thus forming a *dipeptide*. For example the formation of a dipeptide of two molecules of aminoethanoic (glycine) acid may be expressed as follows:



This dipeptide may react with another molecule of aminoethanoic (or another α -amino acid) and so on. The long polypeptides build proteins.

The most important for human organism α -amino acids are a little bit more than 20. Some of them (the so called **essential amino acids**) can not be synthesized by the human body. They must come with food. Therefore the nutritional balance is essential to the body health.

CAN YOU ANSWER THESE QUESTIONS ?

1. What is the functional group of amines?
2. What is the valence of nitrogen in amines and amino acids?
3. Why do amines react with acids?
4. What are the functional groups of amino acids?
5. Why are α -aminopropanoic acid and β -aminopropanoic acid different compounds?
6. What is a peptide bond?
7. What are polypeptides?
8. What are essential amino acids?

PROJECTS

1. USE OF ALCOHOLS AND PHENOLS IN THE EVERYDAY LIFE

Learn about some interesting uses of alcohols and phenols in household. What are alcohols used for? (See for example www.methanol.org)

2. PHYSIOLOGICAL EFFECT OF ETHANOL

Ethanol is a drug (narcotic). Learn what happens in the organism when drinking beer, wine, vodka, whiskey. Why is alcohol abuse destructive?

3. TRIGLYCERIDES

Learn about the physiological role of triglycerides. Why is the level of triglycerides in the blood an important health indicator?

4. PHENOL - A SERIOUS POLLUTANT OF SOIL AND WATER

Learn about the impact of phenol pollution on the environment. What is the effect of contaminated with phenol water on the vital functions of human and animal organisms? What are the major industrial processes that might contaminate soil and water with phenol? How is phenol removed from wasted water? Is there near your town or village an enterprise that might be a potential source of phenol contamination?

5. ALDEHYDES ODOUR

Many aldehydes have a very pleasant odour. They are components of perfumes and some of them (for example vanilla, cinnamon) are used in confectionery. Learn about them.

6. PROPANONE IN NATURE

Is propanone found in nature? What may happen if propanone contaminates water, soil or air? Why should not be thrown out varnishes and dyes in the sewage?

7. CARBOXYLIC ACIDS IN THE EVERYDAY LIFE

Citric acid, malic acid and tartaric acid are used in cookery. What are their chemical formulae and structures? In which fruits do they naturally occur? In which food products do we use them and why?

8. ASPIRIN

Learn about the „history“ of aspirin. How is aspirin synthesized? What are the beneficial effects of aspirin? What are the possible side effects?

9. ESSENTIAL AMINO ACIDS

Which are the essential amino acids? Which foods do contain them? What is the daily need of the organism of these acids? Propose a healthy week menu for your family.