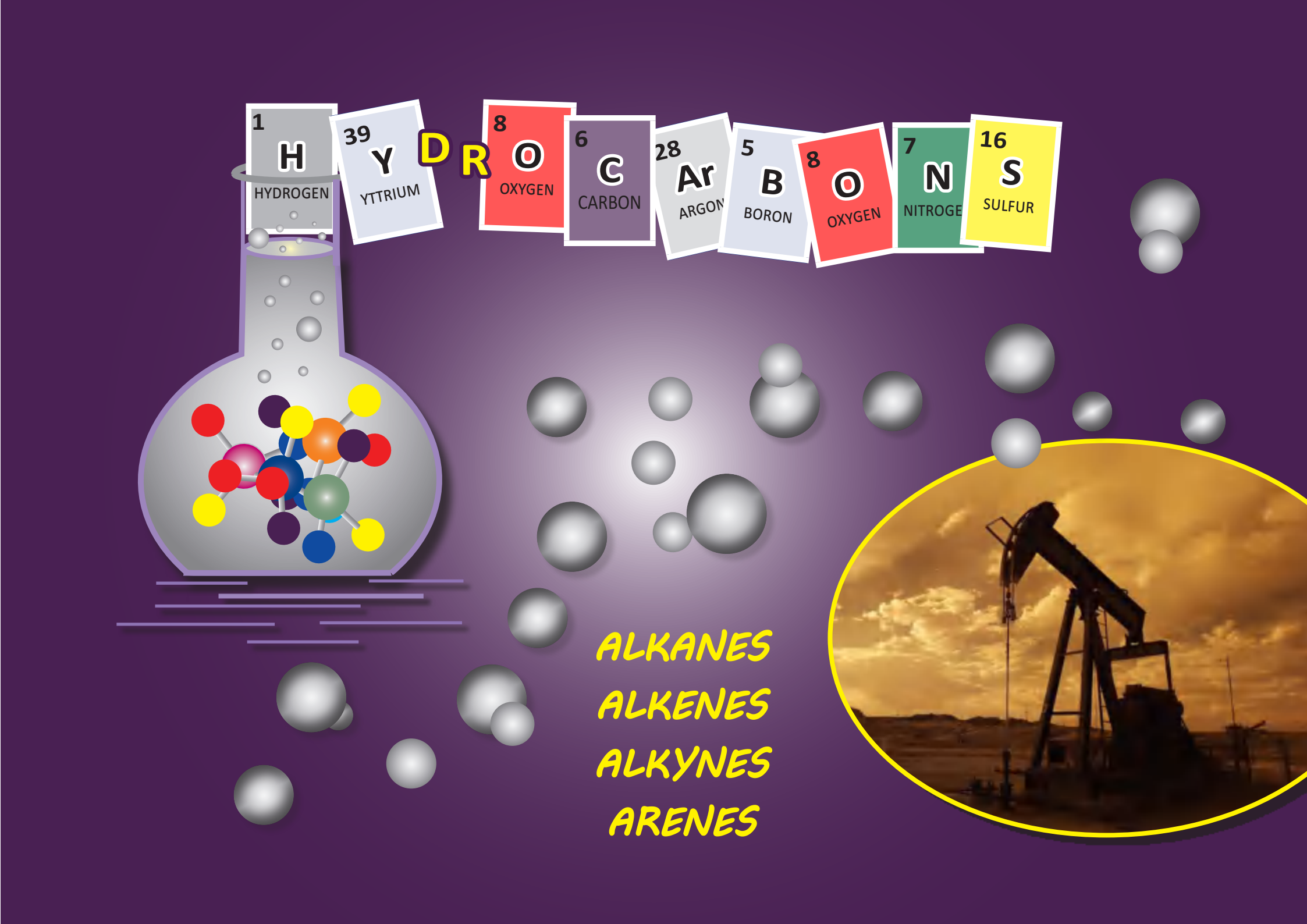

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HYDROGEN
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ARGON
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BORON
8
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OXYGEN
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SULFUR
ALKANES
ALKENES
ALKYNES
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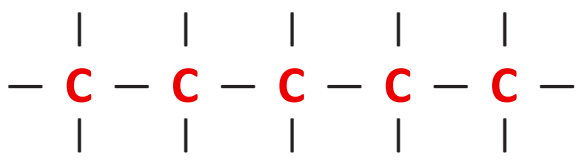
Are we alone in the Universe? There is no answer to this question yet. Up today there is no reason to believe that another civilization or even simple forms of living matter exist somewhere in the Universe. But what scientists really do know is the undisputed fact that the carbon atom is the most important building material of all living organisms on the Earth.

Organic food, organic vegetables, organic materials etc. We often use these terms in our everyday language for different natural products. This is may be a special „slang“ to underline our preferences to the good „natural“ time of our great-grand parents. But in science the term **organic** has a different meaning – it refers to all compounds with carbon in their molecules (except CO, CO_2, H_2CO_3, all carbonates and a few other compounds). The variety of organic compounds and materials is incredible and organic chemistry focuses on the study of their structures, properties, reactions, production. In brief one can say:

ORGANIC CHEMISTRY IS A SCIENCE OF THE CARBON COMPOUNDS.

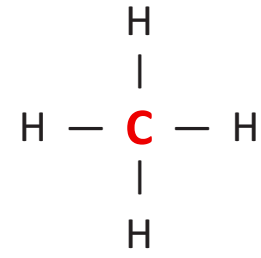
HISTORY

Organic chemistry is a relatively young science. At the end of the XVIIth century Nicholas Lémery proposed to classify the known substances according to their origins (mineral, vegetable and animal). The major milestones of the classical organic chemistry started in the beginning of XIXth century, when Jöns Berzelius introduced the terms *organic chemistry* and *organic compounds*. In that time as organic were considered compounds synthesized only in animals and plants by the action of some mysterious vital force – „vis vitalis“ (life force). During the next decades some organic compounds were synthesized from inorganic raw materials and thus the vitalistic concepts were refuted – first in 1828 Friedrich Wöhler synthesized in his laboratory urea (a final product in the mammals metabolism). After him Nikolai Zinin, Hermann Kolbe, Marcellin Berthelot , Mihail Butlerov also synthesized organic compounds from inorganic substances.



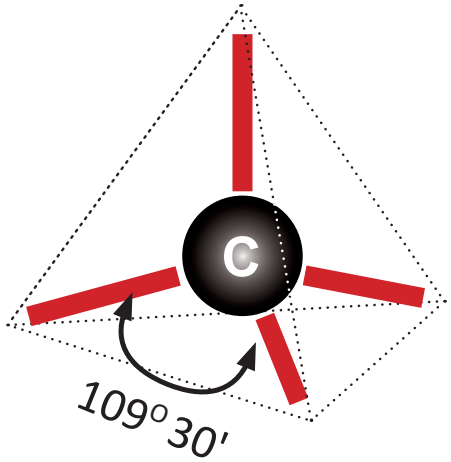
CARBON CHAIN

In the middle of XIXth century Friedrich Kekulé suggested that in organic compounds carbons atoms are always tetravalent. He (and independently Archibald Couper) also concluded that the carbon atoms in the organic compounds can bond to each other, thus forming long carbon chains. Couper proposed to denote the chemical bonds by small lines, connecting the bonding atoms. Thus the graphical presentation of the structure of the compounds (the so called *structural formula*) was introduced.



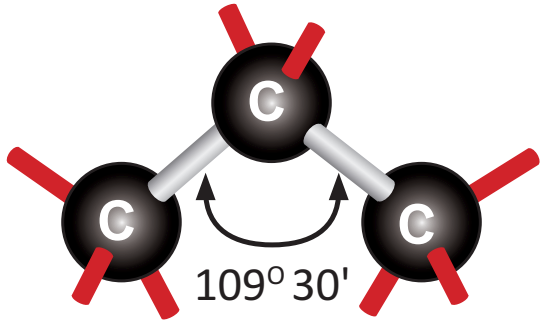
STRUCTURAL FORMULA OF THE SIMPLEST ORGANIC COMPOUND METHANE CH_4

In 1861 Aleksander Butlerov formulated the main concepts of the theory of structure of compounds (known as Structural theory). It emphasizes the strong relation between the properties of the compounds (organic and inorganic) and the structure of their molecules.



THE TETRAVALENT CARBON ATOM

In the late 70s of the XIXth century Jacobus van't Hoff (the first laureate of the Nobel prize in chemistry) and independently Joseph Le Bel assumed that the valences of the carbon atom were directed towards the vertices of a regular tetrahedron and the carbon atom itself was located in the centre of the tetrahedron. This concept is the basis of the understanding of the spatial (three dimensional) structure of the organic compounds.



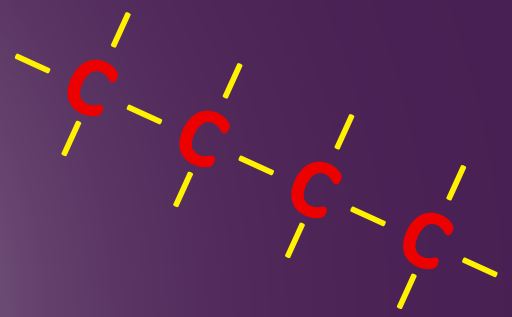
3-CARBON ATOMS CHAIN

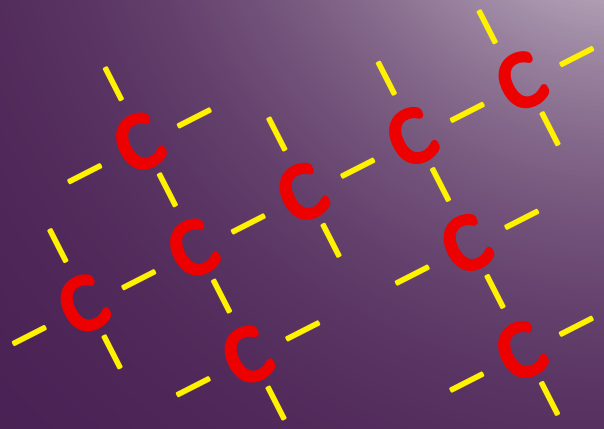
The modern organic chemistry is based on the concepts of the quantum mechanics and is a rapidly progressing science. Up today more than 10 millions organic compounds are known and organic chemistry is undoubtedly a science of a huge importance for the humanity.

25 Organic compounds. Structure and composition

KEY TOPICS

1. What makes the carbon atom so unique?
2. What is a carbon chain?
3. What is an open and a closed carbon chain?
4. What is a branched carbon chain?
5. What are isomers?





KEY WORDS

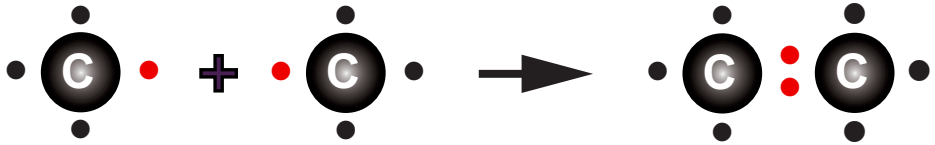
- Tetravalent carbon atom
- Catenation
- Carbon chain
- Open (straight, linear) chain
- Branched chain
- Closed (cyclic, ring) chain
- Isomerism
- Isomers

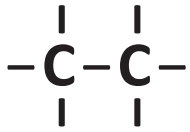
HOW DO CARBON ATOMS FORM CARBON CHAINS?

In all organic compounds carbon atoms are in excited state (see chapter „Carbon atom and its inorganic compounds“, p. 6) and use all their 4 valence electrons to bonds to other carbon atoms or atoms of other chemical elements (more often nonmetals – hydrogen, oxygen, halogens etc.). So:

CARBON IS TETRAVALENT IN ALL ORGANIC COMPOUNDS.

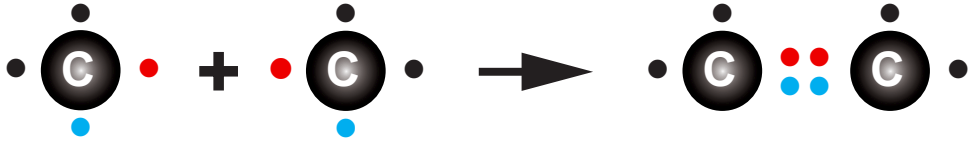
Carbon atoms bond to one another using one, two or three of their valence electrons thus forming single, double or triple nonpolar covalent bonds. The simplest is the single carbon-carbon bond – two single electrons (one from each carbon atom) form a shared electron pair:





SINGLE CARBON-CARBON BOND

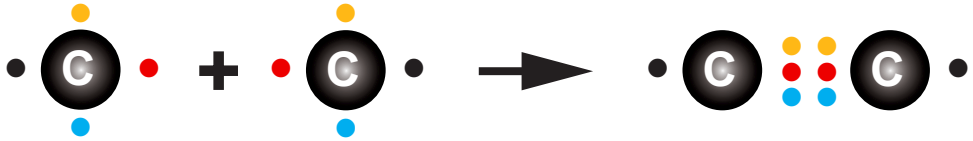
When two carbon atoms bond to one another by a double covalent bond each atom uses two of its valence electrons thus forming two shared electron pairs:





DOUBLE CARBON-CARBON BOND

When two carbon atoms bond to one another by a triple covalent bond each atom uses three of its valence electrons thus forming three shared electron pairs:



$-C \equiv C-$

TRIPLE
CARBON-CARBON BOND

The unused valence electrons form shared electron pairs with other carbon atoms or atoms of other elements (more often halogens, oxygen, nitrogen, etc.)

The chemical linkage into chains of atoms of the same element is named **CATENATION** (self-linking).

Besides carbon, catenation property display also sulfur, silicon, boron, germanium and some other elements but not so well pronounced.

Many (even millions) carbon atoms can link to one another and form carbon chains of different length and shape. As they are the skeleton (the backbone) of each organic compound the variety of these compounds is enormous.

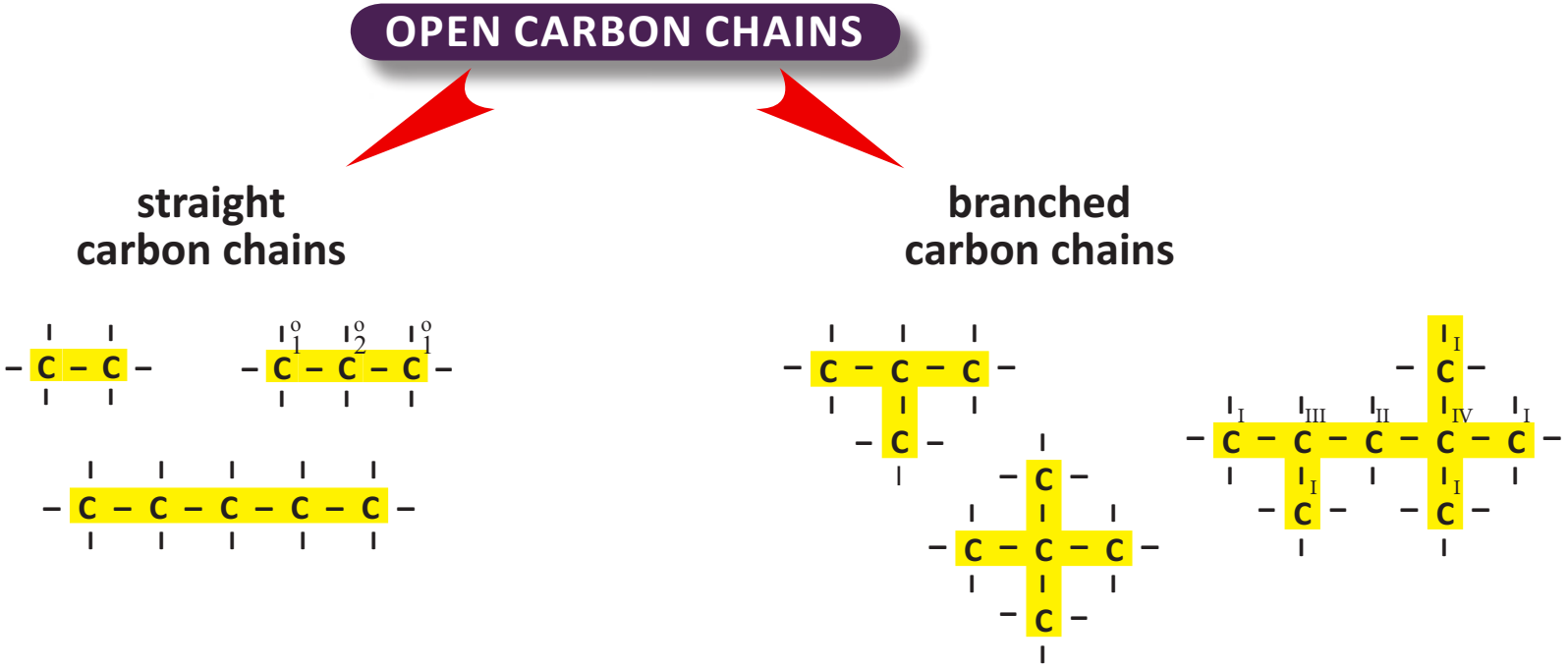
THE GREAT VARIETY OF THE ORGANIC COMPOUNDS IS DUE TO THE ABILITY OF CARBON ATOMS TO FORM VARIOUS CARBON CHAINS OF DIFFERENT LENGTH AND SHAPE.

Depending on their shape the carbon chains are *open* or *closed*, *straight* or *branched*:

OPEN CARBON CHAINS

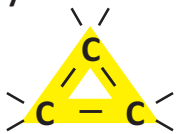
Open carbon chains contain at least two primary (bonded to only one carbon atom) C atoms. The primary C atoms are denoted by the symbol „$\overset{\circ}{1}$“ or by the Roman numeral „I“, written above the chemical symbol of the carbon atom. The open chains contain also secondary (bonded to two C atoms), tertiary (bonded to three C atoms) and quaternary (bonded to four C atoms) carbon atoms. They are denoted by the symbols „$\overset{\circ}{2}$“, „$\overset{\circ}{3}$“ and „$\overset{\circ}{4}$“ respectively or by the corresponding Roman numerals („II“, „III“, „IV“).

Carbon chains formed only by primary and secondary C atoms are straight (called also linear). The branched carbon chains contain additionally tertiary and/or quaternary C atoms:

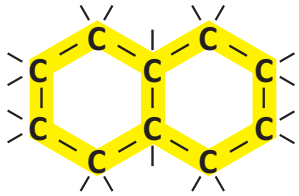


CLOSED CARBON CHAINS

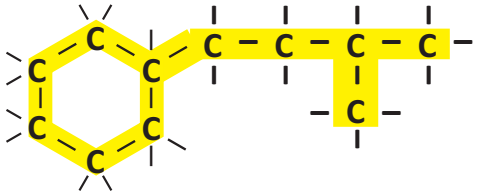
The closed (also called cyclic or ring) carbon chains do not contain primary C atoms. The bonded C atoms form rings. The simplest closed chain is formed by three C atoms:



The rings may be bonded to other rings and/or to straight or branched chains:



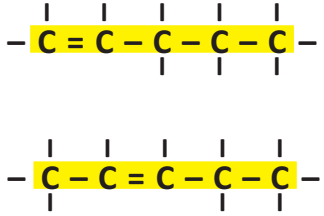
Carbon chain with two rings



6-atomic ring bonded to a branched chain of 5 C atoms

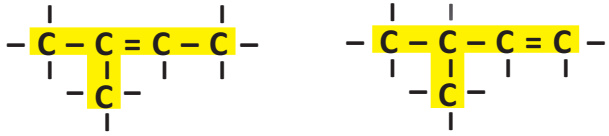
The adjacent C atoms in the carbon chains my be bonded to each each other not only be simple (single) bonds but also by multiple (double or triple) bonds:

a



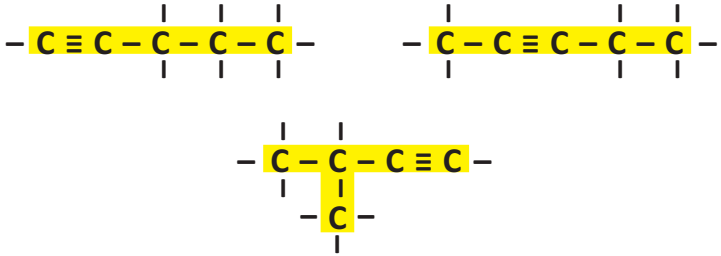
Open straight chains of 5 C atoms with one double bond

b



Open branched chains of 5 C atoms with one double bond

c

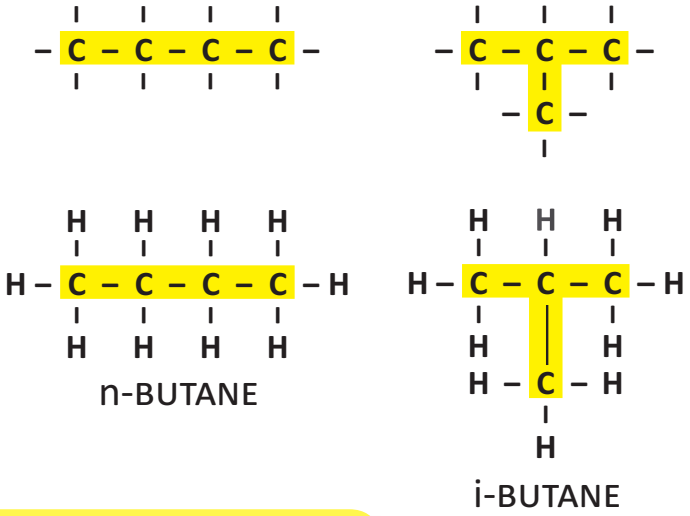


Open chains of 5 C atoms with one triple bond

ISOMERISM

According to the modern scientific concepts, based on the structural theory, the properties of molecules depend not only on the number and the type of atoms but also on their arrangement. Thus different compounds can have the same chemical formula but different properties as the atoms in their molecules form different patterns. This phenomenon is known as isomerism.

For example 4 carbon atoms can form two different open chains – one straight and one branched. These chains are the skeleton of two different compounds built up of carbon and hydrogen atoms. The molecular formula of both compounds is the same – C_4H_{10}, but the boiling point of the straight chain compound (n-butane) is -0,6 °C, while the compound with a branched chain (i-butane) boils at -11,7 °C. So these are two different compounds. Such compounds are called **isomers**.

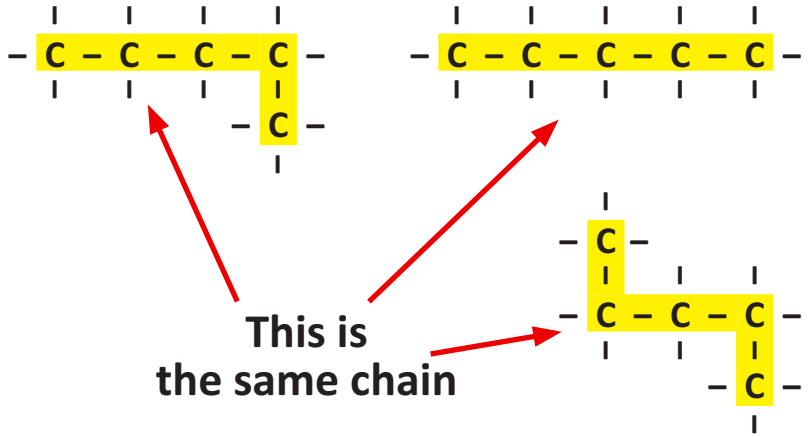


ISOMERS ARE CHEMICAL COMPOUNDS WITH THE SAME MOLECULAR FORMULA BUT DIFFERENT ARRANGEMENTS OF THE ATOMS.

Thus if the carbon atoms of the chains **a** and **b** from the previous page bond only to hydrogen atoms these carbon chains build the molecules of four different compounds represented by the same chemical formula C_5H_{10}. These compounds are isomers. It is the same for the chains **c** but the chemical formula of the three compounds is C_5H_8.

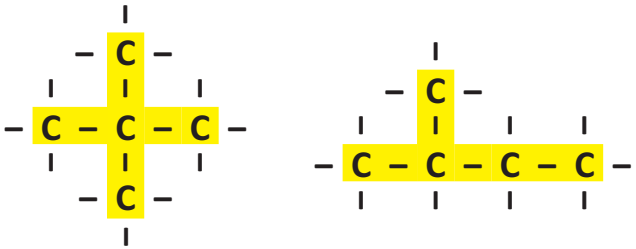
Two main types of isomers are the chain isomers and the position isomers:

CHAIN ISOMERS are compounds with the same molecular formula but *different arrangement of the carbon atoms in the carbon chains*. This type of isomerism is due to the branching of the carbon skeleton. n-butane and i-butane (shown above) are chain isomers. Keep in mind that branching occurs only if the chain contains at least one tertiary or one quaternary C atom. For instance, in the picture below is illustrated the carbon skeleton of the compound C_5H_{12} (the name is pentane) with a straight carbon chain:



STRAIGHT CARBON CHAIN OF C_5H_{12}

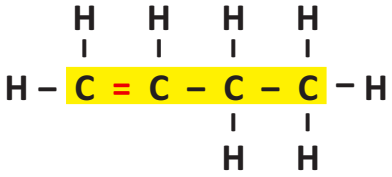
The carbon chains of its Isomers are:

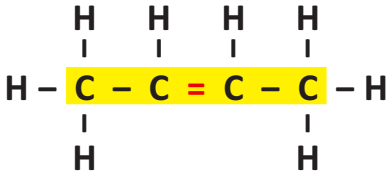


BRANCHED CARBON CHAINS OF THE ISOMERS OF C_5H_{12}

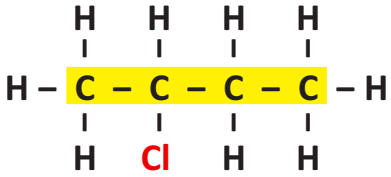
The number of chain isomers rises rapidly with the increase of the number of C atoms building them. So the isomers of $C_{40}H_{82}$ are more than 60 trillions!

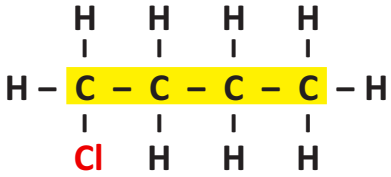
POSITION ISOMERS are compounds with the same molecular formula but *different positions of multiples bonds* or *different positions of functional groups* (atom or group of atoms that are essential to the reactivity of the compound):



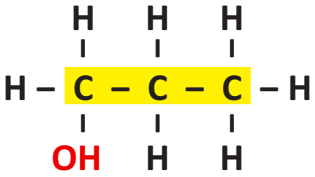


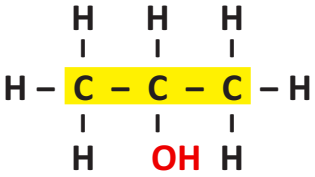
Position isomers of butene C_4H_8





Position isomers of chlorobutaneC_4H_9Cl





Position isomers of propanol C_3H_7OH

The chains **a** (p. 10) represent the skeletons of two position isomers of the open chain compound C_5H_{10}. It is the same for chains **b** but the skeleton is branched. The chains **c** represent the skeleton of two position isomers and one chain isomer of the compound C_5H_8.

The isomers always display specific properties. So they are different chemical compounds.

CAN YOU ANSWER THESE QUESTIONS ?

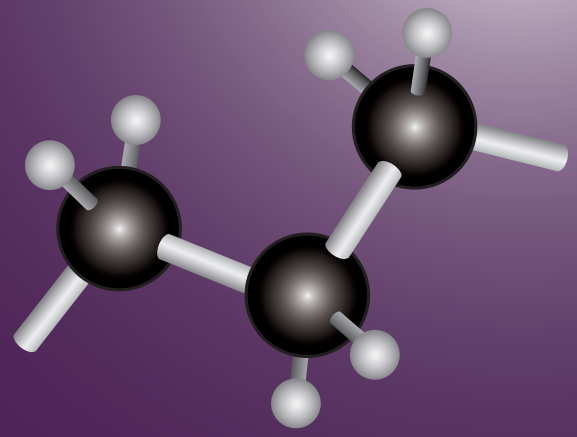
1. Are there organic compounds without carbon in their molecules?
2. Are there organic compounds in which carbon is divalent?
3. Why are there so many (millions) organic compounds known up today?
4. How many carbon atoms are linked in the shortest branched carbon chain?
5. What are isomers?
6. What is a chain isomer and what is a position isomer?
7. Does the compound C_2H_6 have chain isomers?

26 Hydrocarbons. Alkanes

KEY TOPICS

1. What are hydrocarbons?
2. Why are alkanes the simplest hydrocarbons?
3. What is a homologues series?
4. How to name alkanes?
5. Are alkanes reactive compounds?

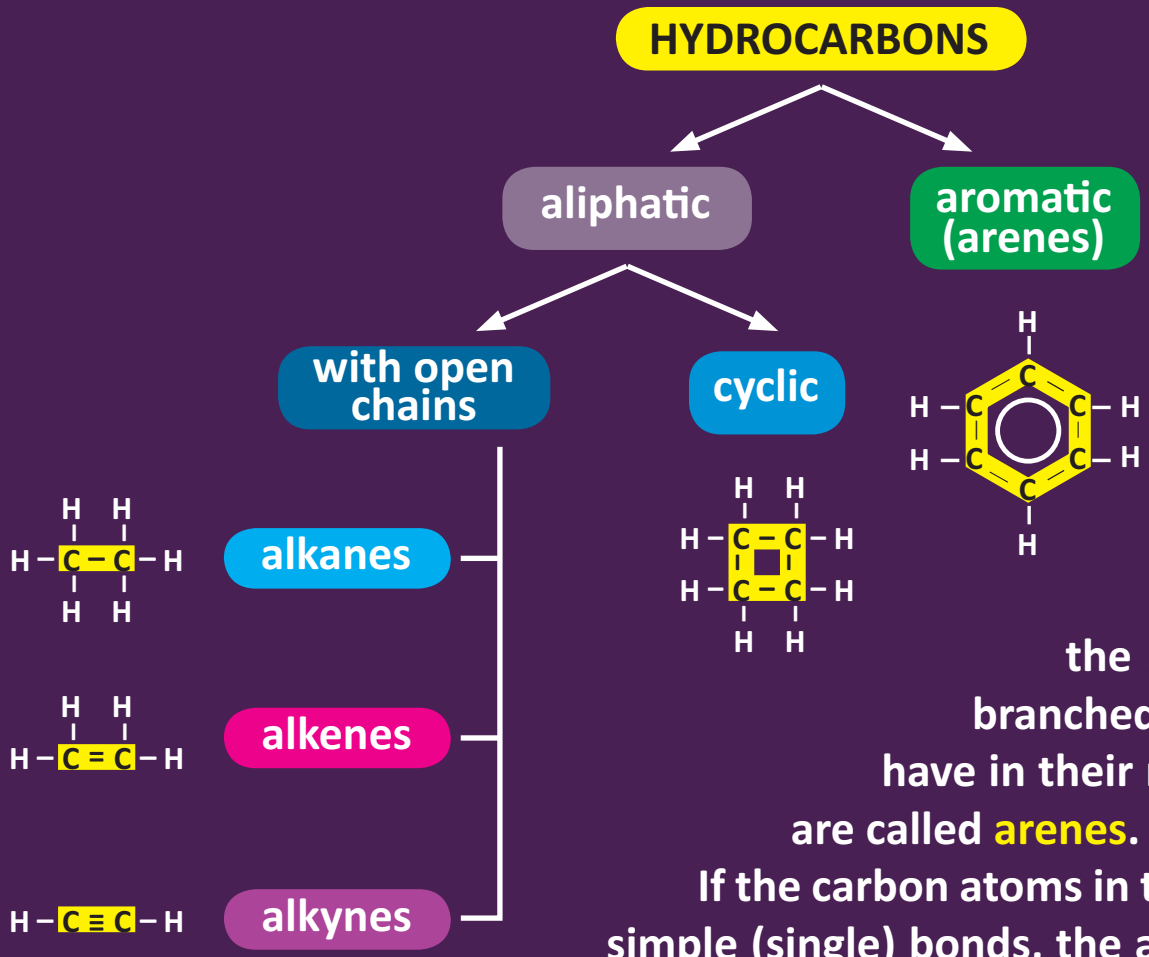
C_nH_{2n+2}



KEY WORDS

- Hydrocarbons
- Alkanes
- Bond-line structure
- Homologues series
- Homologues
- Methylene group
- Alkyl group
- Radicals

HYDROCARBONS – A MAJOR CLASS OF ORGANIC COMPOUNDS



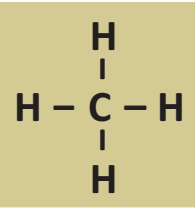
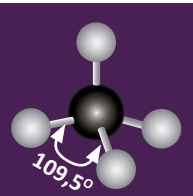
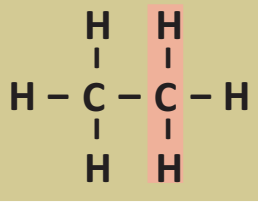
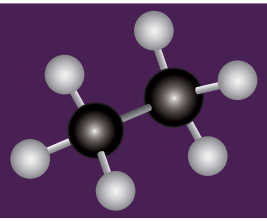
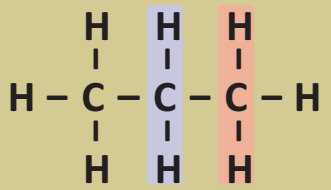
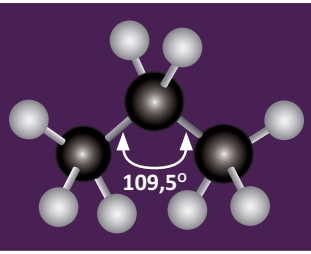
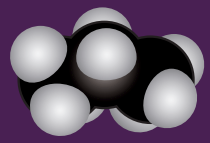
Hydrocarbons are the simplest organic compounds. They are the most abundant organic compounds in non-living nature. As their name suggests, these compounds are composed of carbon and hydrogen.

HYDROCARBONS ARE COMPOUNDS OF CARBON AND HYDROGEN.

Depending on the structure of their carbon skeleton the hydrocarbons are classified as **aliphatic** and **aromatic**. The carbon chains of the aliphatic hydrocarbons are open (straight or branched) or closed (cyclic). All aromatic hydrocarbons have in their molecules a specific 6-carbon atoms ring and are called **arenes**.

If the carbon atoms in the carbon chain bond to one another only by simple (single) bonds, the aliphatic hydrocarbons are **saturated** (contain the maximum number of hydrogen atoms). If two or more adjacent C atoms are linked by multiple (double or triple) bonds, the aliphatic hydrocarbons are **unsaturated**. The saturated hydrocarbons are named **alkanes**. The unsaturated hydrocarbons with a double carbon-carbon bond are named **alkenes** and those with a triple carbon-carbon bond – **alkynes**.

ALKANES are the simplest hydrocarbons. All carbon-carbon bonds in their molecules are single covalent bonds. They are not very reactive compounds and for this reason they are also known as *paraffins* (in Latin language *parum affinis* means *low affinity*). Their properties depend on the number of C atoms in their molecules and on the structure of the carbon chains. In the table below are shown the molecular formulae, the structural formulae (also the so called condensed formulae) and the ball-and-stick and space-filling models of the simplest alkanes – methane, ethane and propnane:

NAME	Molecular formula	Structural formula	Condensed formula	MODEL ball-and-stick	MODEL space-filling
METHANE	CH_4		CH_4		
ETHANE	C_2H_6		$CH_3 – CH_3$		
PROPANE	C_3H_8		$CH_3 – CH_2 – CH_3$		

H atom C atom

In the ethane molecule C_2H_4 there are one C atom and two H atoms more than in the methane molecule CH_4. It is the same if we compare the compositions of ethane C_2H_4 and propane C_3H_8 – propane contains one C atom and two H atoms more than ethane. The atomic group $>CH_2$ is called methylene group (one C atom covalently bonded to two H atoms).

If we arrange all alkanes in ascending order of the number of C atoms in their molecules, a series of similar hydrocarbons is formed. Each alkane in this series contains one methylene group more than the previous one and one methylene group less than the successive one:

$$CH_4,\ C_2H_6,\ C_3H_8,\ C_4H_{10},\ C_5H_{12},\ C_6H_{14}\ \ldots\ldots\ldots\ldots\ C_{20}H_{42},\ C_{21}H_{44},\ C_{22}H_{46}\ \ldots\ldots$$

The composition of all members of the series is expressed with the general formula C_nH_{2n+2} (*n* is the number of C atoms in the molecule). Such a series of similar compounds is called a homologous series and the compounds – homologues.

A SERIES OF ORGANIC COMPOUNDS WITH SIMILAR STRUCTURE AND COMMON GENERAL FORMULA, IN WHICH THE COMPOSITION OF EACH MEMBER DIFFERS FROM THE NEXT MEMBER BY A METHYLENE GROUP $>CH_2$, IS CALLED A HOMOLOGOUS SERIES.

MEMBERS OF A HOMOLOGOUS SERIES ARE CALLED HOMOLOGUES.

PROBLEM!

Express the molecular formulae of the alkanes with 4 and 5 carbon atoms in their molecules.

SOLUTION: The general formula of both alkanes is C_nH_{2n+2}:

1. If there are 4 C atoms in the molecule of an alkane n = 4.
   The number of H atoms in its molecule is calculated from the general formula and is:
   $2n + 2 = 2.4 + 2 = 10$ H atoms.
2. If there are 5 atoms in the alkane molecule n = 5 and the number of H atoms is:
   $2n + 2 = 2.5 + 2 = 12$ H atoms.

ANSWER: The molecular formulae of the alkanes with 4 and 5 C atoms are $\mathbf{C_4H_{10}}$ and $\mathbf{C_5H_{12}}$.

ISOMERS OF ALKANES

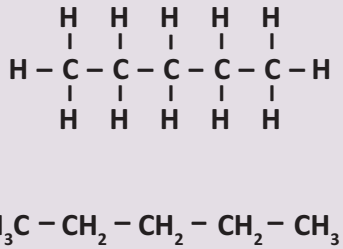
Alkanes with more than 3 carbon atoms have chain isomers – their carbon skeleton may be straight or branched. For example butane C_4H_{10} has two isomers – one with a straight chain and another one with a branched chain (see p. 11). There are milliards of possible structures of the carbon chains of the alkane $C_{30}H_{62}$ and trillions of possible isomers of $C_{40}H_{82}$.

C_7H_{16}	9 isomers
C_8H_{18}	18 isomers
C_9H_{20}	35 isomers
$C_{10}H_{22}$	75 isomers
$C_{20}H_{42}$	> 300 000 isomers
$C_{30}H_{64}$	> 4.10^9 isomers
$C_{40}H_{84}$	> 6.10^{13} isomers

PROBLEM!

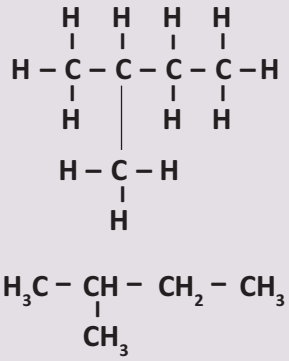
Express the structural and the condensed formulae of the chain isomers of the alkane with 5 C atoms (C_5H_{12}).

SOLUTION:

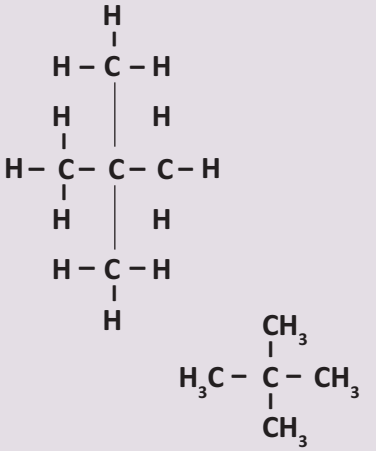


$H_3C - CH_2 - CH_2 - CH_2 - CH_3$

or $H_3C - (CH_2)_3 - CH_3$

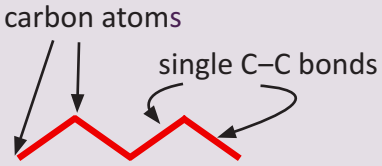


$H_3C - CH(CH_3) - CH_2 - CH_3$



$H_3C - C(CH_3)_2 - CH_3$

Can be simplified as:







The bond-line structure represents only the compound skeleton (remember that the C – C bond angle is 109,5° and the carbon chain makes a zigzag line). Each end point and each bend represents one C atom. The short lines, connecting the C atoms, represent the bonds in the molecule.

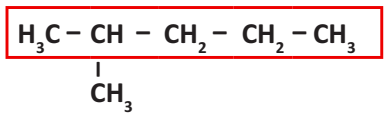
HOW TO NAME ALKANES?

The first four homologues are known with their common names: *methane* CH_4, *ethane* C_2H_6, *propane* C_3H_8 and *butane* C_4H_{10}. According to the IUPAC (**I**nternational **U**nion of **P**ure and **A**pplied **C**hemistry) recommendations the names of the alkanes with *straight chains* of 5 and more carbon atoms are formed from the root of the Greek name of the numeral indicating the number of carbon atoms in the molecule and the suffix „-ane“. To distinguish between isomers of an alkane the straight chain isomer is called normal. This is indicated with the letter „n“ written before the name of the alkane. For example n-butane ($CH_3-CH_2-CH_2-CH_3$)

CH_4	methane
C_2H_6	ethane
C_3H_8	propane
C_4H_{10}	butane
C_5H_{12}	pentane
C_6H_{14}	hexane
C_7H_{16}	heptane
C_8H_{18}	octane

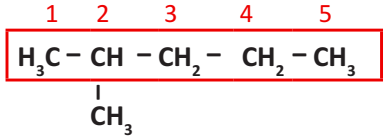
The *branched chain alkanes* are named according to the IUPAC recommendations as follows:

RULE 1.
The longest straight carbon chain gives the name of the alkane (indicated in the red box).

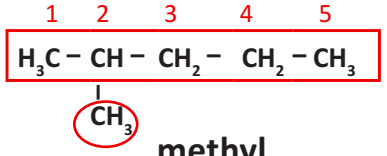


pentane

RULE 2.
The carbon atoms in the straight chain are numerated so that the branch to be located as near as possible to the end of the chain.



RULE 3.
The branch name is formed using the name of the alkane with the same number of C atoms as in the branch. The suffix „-ane“ is replaced by the suffix „-yl“(–CH_3 methyl, –C_2H_5 ethyl etc.).



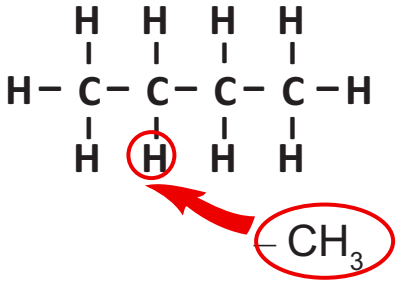
methyl

RULE 4.
The branch name is written before the name of the alkane. Its place is indicated by the number of the carbon atom to which it is attached, followed by a dash.

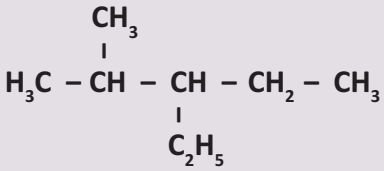
2-methylpentane

The atomic groups $-CH_3$, $-C_2H_5$ etc. are called alkyl groups or radicals. They contain 1 H atom less than the corresponding alkanes. One alkyl group substitutes one H atom bonded to a C atoms from the main chain.

If there are two or more different branches, they are listed in alphabetic order.

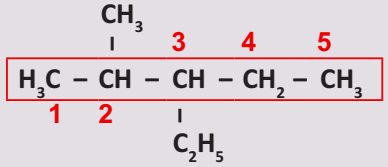


PROBLEM! **Name the alkane:**



SOLUTION: **1.** The longest straight carbon chain has 5 C atoms – the hydrocarbon is a branched **pentane**.

2. The carbon atoms in the straight chain are numerated so that the branch to be located as near as possible to the end of the chain.



3. The branches names are formed using the name of the alkanes with the same number of C atoms as in the branches replacing the suffix „-ane“ by the suffix „-yl“:

methane → methyl ethane → ethyl

The branches names are „methyl“ and „ethyl“.

4. Their places are indicated by the number of the carbon atom to which they are attached, followed by a dash: 2-methyl and 3-ethyl. They must be listed in alphabetic order „3-ethyl-2-methyl“ before the name of the alkane.

ANSWER: The name of the alkane is **3-ethyl-2-methylpentane.**

If in the carbon chain there are two or more identical branches the prefixes „di-“, „tri-“, „tetra-“ etc. are added.

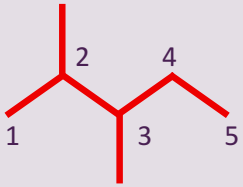
PROBLEM! **Draw the bond-line structure of 2,3-dimethylpentane.**

SOLUTION: The longest straight carbon chain has 5 C atoms:



One methyl group $-CH_3$ is bonded to the second C atom and one – to the third C atom.

ANSWER: The bond-line structure of **2,3-dimethylpentane** is:



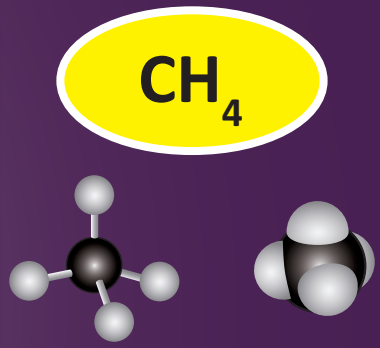
CAN YOU ANSWER THESE QUESTIONS ?

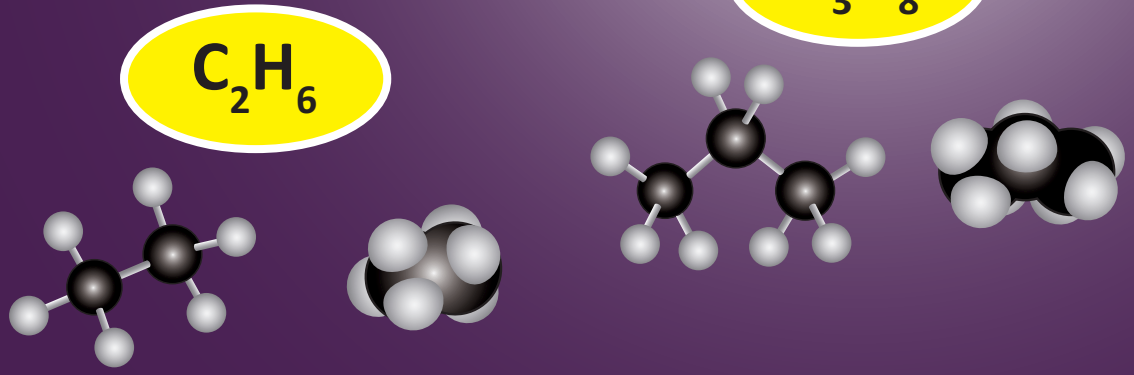
1. What are hydrocarbons?
2. What are alkanes?
3. Why are alkanes saturated hydrocarbons?
4. How are formed the names of n-alkanes?
5. What is the name of the alkane with a straight 8-carbon atoms chain?
6. Are the names of an alkane isomers identical?
7. Why is the alkane name 2-ethyl-1,3-dimethylpropane wrong? What is the correct name?

27 Methane. Ethane. Propane

KEY TOPICS

1. What are the physical and chemical properties of alkanes?
2. What is a substitution reaction?
3. What are freons?
4. Why are low molecular weight alkanes fuels?



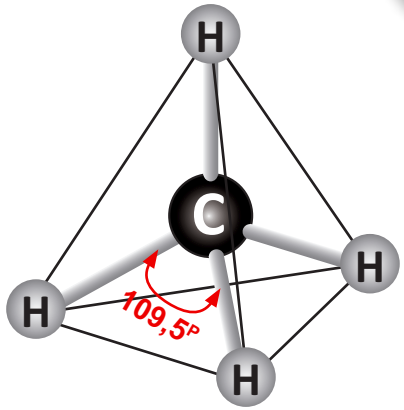


KEY WORDS

- Substitution reaction
- Derivatives of alkanes
- Halogenataion
- Haloalkanes (alkyl halides)
- Freons
- Combustion

Methane CH_4 is the simplest alkane, the simplest hydrocarbon and the simplest organic compound. In its molecules the carbon atom is in the centre of a regular tetrahedron while the four hydrogen atoms are located at the vertices of the tetrahedron. The angle between the C – H bonds is 109,5°.

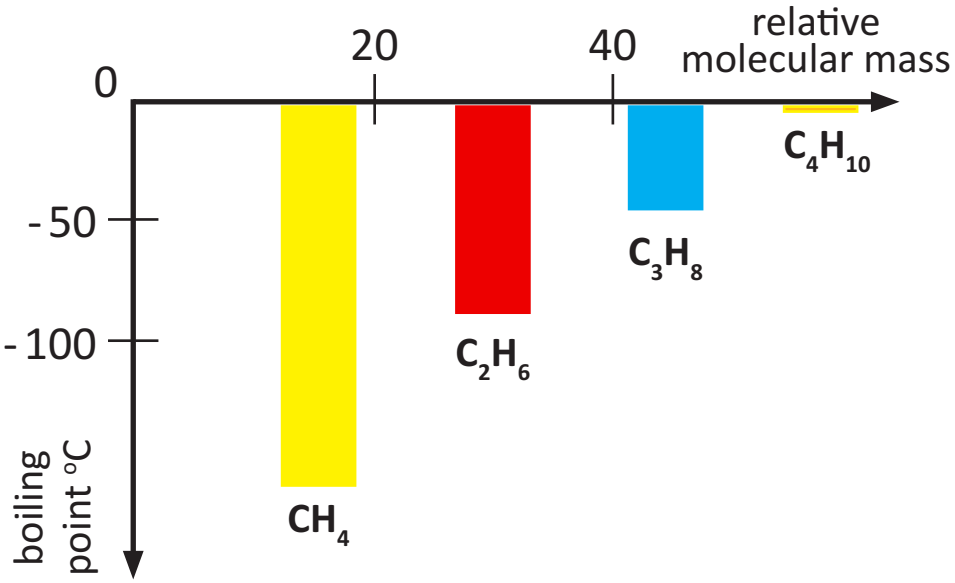
The natural gas contains 80 – 98 % methane and smaller quantities of ethane, propane and butane. Methane is also a product of the natural anaerobic digestion of organic compounds. The firedamp, the marsh gas consist primary of methane.



METHANE CH_4

PHYSICAL PROPERTIES

At standard conditions the first four homologues of alkanes are gases. Methane boils at the lowest temperature. With the increase of the number of C atoms the boiling point raises – butane is the last homologue of the alkane series which is a gas at standard conditions. The next homologues are liquids with a specific odour (of petrol). Alkanes with straight chains of 14 and more C atoms are solids at standard conditions.



Methane, ethane, propane and butane are colourless and odourless gases. For safety, odorants are added to the mixture of propane and butane for domestic uses.

All alkanes are insoluble in water.

CHEMICAL PROPERTIES

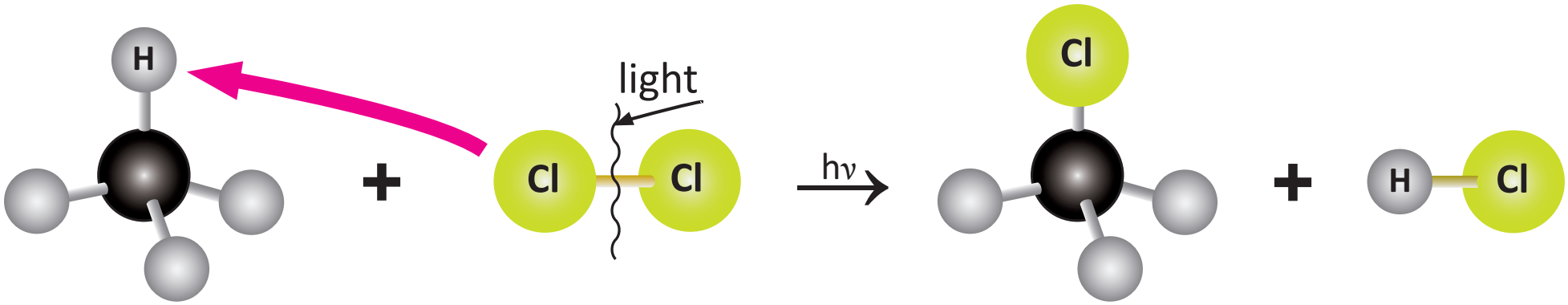
Alkanes are not very reactive compounds but under specific conditions C – C or C – H bonds break down. It is easier to disrupt the C – H covalent bond. The hydrogen atom is substituted by an atom of another element or by an atomic group. The products of these reactions are considered as derivatives of alkanes. These reactions are called substitution reactions.

SUBSTITUTION REACTIONS ARE CHEMICAL REACTIONS IN WHICH AN ATOM, OR GROUP OF ATOMS IN A MOLECULE, IS REPLACED BY ANOTHER ATOM OR GROUP OF ATOMS.

A typical substitution reaction for alkanes is the halogenation – interaction with halogens (the VIIA group elements). The products haloalkanes are also known as alkyl halides.

HALOGENATION OF METHANE

The reaction of methane with fluorine is vigorous – the mixture of methane and fluorine explodes even at STP. On the other hand iodine does not react with methane at all. The reactions with chlorine and bromine undergo only when the gases mixture is exposed to sunlight. The Cl – Cl bond is broken down and chlorine atoms are capable to replace hydrogen atoms in the methane molecule. As a result chloroderivatives of methane are obtained. First 1 H atom is substituted and the product is chloromethane:



CH_4 + Cl_2 → CH_3Cl + HCl

methane — **chloromethane**

If there is enough chlorine Cl_2 in the gaseous reaction mixture the reaction continues and two, three or all four H atoms in the methane molecule can be substituted by chlorine atoms:

$$\underset{\text{chloro-methane}}{CH_3Cl} \xrightarrow{Cl_2} \underset{\text{dichloro-methane}}{CH_2Cl_2} \xrightarrow{Cl_2} \underset{\text{trichloro-methane}}{CHCl_3} \xrightarrow{Cl_2} \underset{\text{tetrachloro-methane}}{CCl_4}$$

Trichloromethane is also known as *chloroform*.

COMBUSTION OF ALKANES

Alkanes burn at high temperature. Carbon dioxide and water are produced and energy is released. For this reason the natural gas is used as a fuel in the industry as well as in household.

The reaction of the complete combustion of methane is:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{energy}$$

PROBLEM! **How many moles of carbon dioxide CO_2 are produced in the combustion of 1 mol of propane C_3H_8?**

SOLUTION: **1.** The balanced chemical equation of the reaction of combustion of propane is:

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

2. The molar ratio of C_3H_8 and CO_2 is: $n(C_3H_8) : n(CO_2) = 1 : 3$

So $n(CO_2) = 3n(C_3H_8)$ and for $n(C_3H_8) = 1$ mole we obtain $n(CO_2) = 3$ moles.

ANSWER: In the combustion of 1 mol C_3H_8 are produced **3 moles of CO_2**.

The combustion of fossil fuels is a major source of atmospheric CO_2 – a prominent greenhouse gas. In the molecules of methane and the other gaseous alkanes there are only 1 to 4 C atoms. So the harmful emissions released into the air from the combustion of 1 mole of these gases are much less than the emissions from long-chain liquid or solid fossil fuels. But methane itself is a greenhouse gas too.

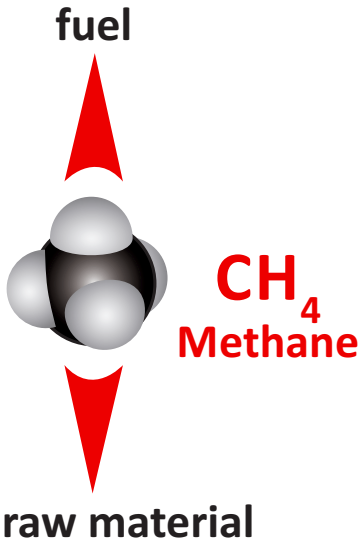
Methane (as well as the other gaseous alkanes (ethane, propane and butane) and the vapours of the volatile liquid alkanes) is a flammable gas. Mixed with pure oxygen or air it is highly explosive. Spark or flame can provoke dangerous explosions and safety precautions must be respected. Methane is nontoxic, but the halomethanes are toxic and their vapours should not be inhaled. Ethane has a weak narcotic effect.



HAZARD SYMBOL FOR A FLAMMABLE SUBSTANCE

USES

Alkanes are used as fuels and as raw materials in the organic synthesis. Dichloromethane CH_2Cl_2, trichloromethane $CHCl_3$ and tetrachloromethane CCl_4 are organic solvents. At high temperature methane decomposes into hydrogen and soot used as a filler to improve polymers quality.



FREONS are haloalkanes, mainly derivatives of methane and ethane: CF_2Cl_2, $CFCl_3$, $CHFCl_2$, $C_2Cl_2F_4$, $C_2Cl_3F_3$, etc. They are refrigerants and are used as aerosol propellants. These compounds decompose under the action of the UV-rays in the stratosphere. The liberated Cl atoms are very reactive – they destroy the ozone molecules:

$$2O_3 \xrightarrow{Cl} 3O_2$$

That results in a considerable ozone layer depletion. This phenomenon is very dangerous because the cosmic ultraviolet radiation reaches the surface of the Earth and may damage all living organisms. That is why the use of freons must be limited.

PRODUCTION

The main sources of gaseous alkanes are the natural gas, the petroleum gas, the biogas.

In the laboratory methane is synthesized from aluminum carbide in its reaction with water or in a reaction of hydrogen with carbon dioxide or carbon monoxide in the presence of catalysts*:

$$Al_4C_3 + 12H_2O \rightarrow 3CH_4\uparrow + 4Al(OH)_3$$

$$CO_2 + 4H_2 \xrightarrow{cat.} CH_4\uparrow + 2H_2O$$

$$CO + 3H_2 \xrightarrow{cat.} CH_4\uparrow + H_2O$$

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

It is interesting to know:

A common way to produce alkanes (except methane) is the Würtz's reaction – two alkyl halides are coupled in a reaction with sodium Na. For example propane is prepared from chloromethane CH_3Cl and chloroethane C_2H_5Cl:

$$CH_3Cl + 2Na + ClC_2H_5 \rightarrow C_3H_8 + 2NaCl$$

choromethane — chloroethane — propane

n-butane C_4H_{10} can be prepared from chloromethane and 1-chloropropane (the chlorine atom has substituted one hydrogen atom bonded to the first carbon atom of the carbon chain) or only from chloroethane:

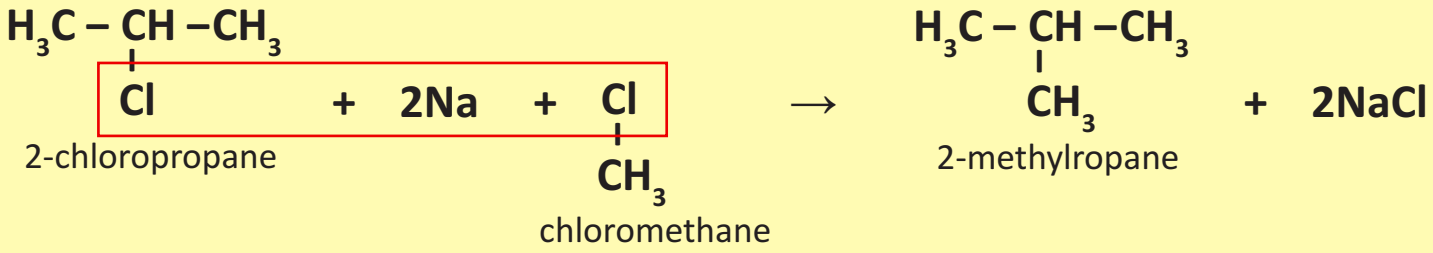
$$CH_3Cl + 2Na + ClCH_2{-}CH_2{-}CH_3 \rightarrow C_4H_{10} + 2NaCl$$

choromethane — 1-chloropropane — n-butane

$$CH_3{-}CH_2Cl + 2Na + ClCH_2{-}CH_3 \rightarrow C_4H_{10} + 2NaCl$$

chloroethane — chloroethane

The isomer of n-butane 2-methylpropane can be synthesized from 2-chloropropane (the chlorine atom has substituted one hydrogen atom bonded to the second carbon atom of the carbon chain) and chloromethane:



2-chloropropane — chloromethane — 2-methylropane

CAN YOU ANSWER THESE QUESTIONS ?

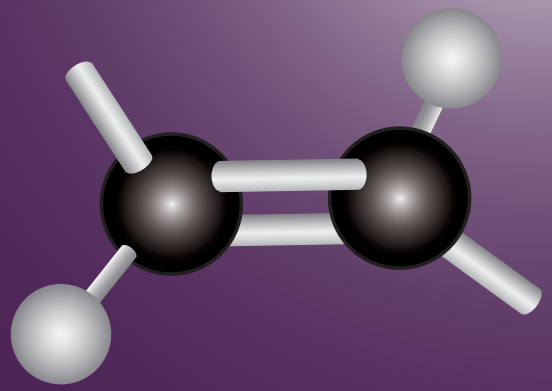
1. Why are methane, ethane and propane homologues?
2. Are propane and methylethane two different names of the same compound? Why?
3. At standard conditions methane CH_4 is a gas insoluble in water while chloroform $CHCl_3$ is a soluble in water volatile liquid. Why?
4. What type of reaction is the production of CH_3Cl from CH_4 and Cl_2?
5. Why should we always read and follow the manufacturer's safety recommendations when using gas bottles?
6. Why are gaseous alkanes attractive fuels?
7. Have you any idea what is the annual world gas consumption?

28 Alkenes

KEY TOPICS

1. What are alkenes?
2. Why do alkenes have position isomers?
3. How to name alkenes?
4. Why do straight chains alkenes form a homologous series?
5. Are alkenes more reactive than alkanes?

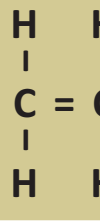
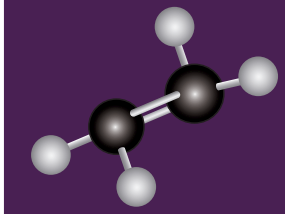
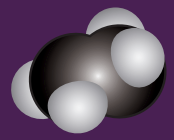
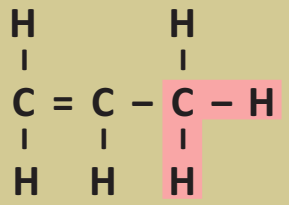
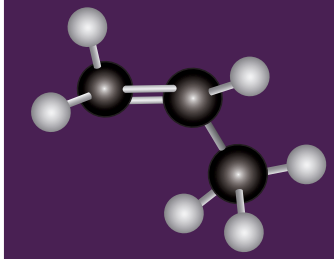
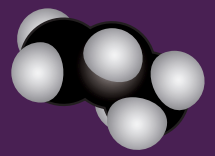
C_nH_{2n}



KEY WORDS

- Alkenes
- Double bonded C atoms
- Homologous series of n-alkenes
- Chain isomers of alkenes
- Position isomers of alkenes

ALKENES are unsaturated hydrocarbons with a double carbon-carbon bond $>C=C<$. They are also known as *olefins* (from Latin language – *oleum* means *oil* and *affinis* means *close to*). Similarly to the alkanes, the straight chain alkenes form a homologous series. The general formula of alkenes is C_nH_{2n}. The simplest alkene is ethene C_2H_4. In its molecule there are two H atoms less than in the molecule of ethane C_2H_6. The second homologue is propene C_3H_6 with one methyl group $>CH_2$ more than in the ethene molecule:

NAME	Molecular formula	Structural formula	Condensed formula	MODEL ball-and-stick	space-filling	bond-line
ETHENE	C_2H_4		$H_2C=CH_2$			
PROPENE	C_3H_6		$H_2C=CH-CH_3$			

PROBLEM! **Write down the molecular formula of the alkene with 5 C atoms.**

SOLUTION: The general formula of alkenes is C_nH_{2n}.
There are five C atoms in the molecule, so n = 5.
The number of H atoms in its molecule is calculated from the general formula and is:
2n = 2.5 = 10 H atoms.

ANSWER: The molecular formula of the alkene with 5 C atoms is $\mathbf{C_5H_{10}}$.

ISOMERS OF ALKENES

Alkenes with 4 and more C atoms have isomers – *chain* (the carbon chains can be straight or branched) and *position* (the position of the double carbon-carbon bond can change):



CHAIN ISOMERS OF AN ALKENE WITH 4 CARBON ATOMS IN THE MOLECULE C_4H_8 (straight and branched chain)



POSITION ISOMERS OF AN ALKENE WITH 4 CARBON ATOMS IN THE MOLECULE C_4H_8 (straight chains)

HOW TO NAME ALKENES?

C_2H_4	ethene
C_3H_6	propene
C_4H_8	butene
C_5H_{10}	pentene
C_6H_{12}	hexene
C_7H_{14}	heptene
C_8H_{16}	octene

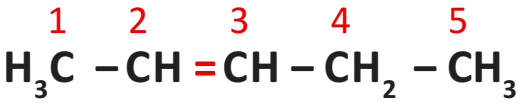
The names of alkenes differ from the names of the alkanes with the same number of C atoms only in the suffix – „-ane“ is replaced by „-ene“. The C atoms are numerated in such a way as to assign to the double bonded C atoms the lowest possible numbers. The number of the first double bonded C atom is written, separated by dashes, before the suffix (or before the name). For example:



propene

The same as

propene



pent-2-ene (or 2-pentene)

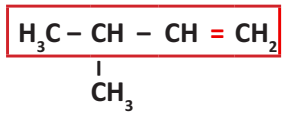
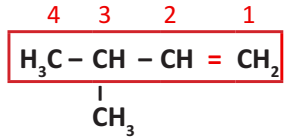
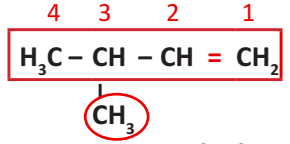
RIGHT



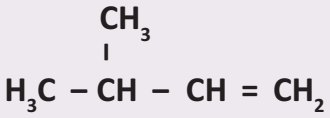
pent-3-ene (or 3-pentene)

WRONG

As for alkanes, the names of alkenes with branched chains are formed according to the IUPAC recommendations:

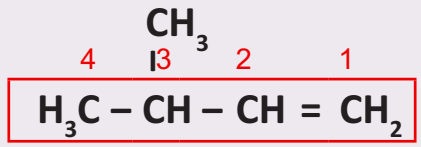
RULE 1. The longest straight carbon chain with the double carbon-carbon bond gives the name of the alkene (indicated in the red box).	 **butene**
RULE 2. The carbon atoms in the straight chain are numerated so that the double bond to be located as near as possible to the end of the chain. Its place is indicated with the number of the first double bonded C atom.	 **but-1-ene** **or 1-butene**
RULE 3. The branch name is formed using the name of the alkane with the same number of C atoms as the branch. The suffix „-ane“ is replaced by the suffix „-yl“ (–CH_3 methyl, C_2H_5 ethyl etc.).	 **methyl**
RULE 4. The branch name is written before the name of the alkene. Its place is indicated by the number of the carbon atom to which it is attached, followed by a dash.	**3-methylbut-1-ene** **or 3-methyl-1-butene**

PROBLEM! **Name the alkene:**



SOLUTION: **1.** The longest straight carbon chain with double bounded C atoms has 4 C atoms – the hydrocarbon is a branched **butene.**

2. The carbon atoms in the straight chain are numerated so that the double bond to be located as near as possible to the end of the chain. Its place is indicated by the number of the first double bonded C atom: **but-1-ene** or **1-butene.**



3. The branch name is formed using the name of the alkane with the same number of C atoms as in the branch replacing the suffix „-ane“ by the suffix „-yl“:

yl

methane

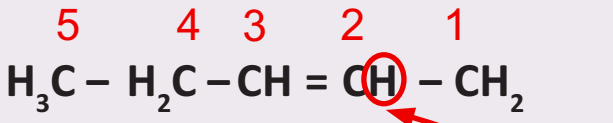
The branch name is „methyl“.

4. Its place is indicated by the number of the carbon atom to which it is attached, followed by a dash: 3-methyl. It is written before the name of the alkene.

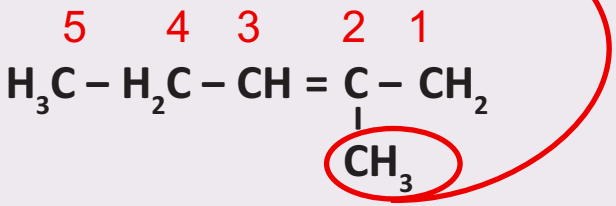
ANSWER: The name of the alkene is **3-methylbut-1-ene** or **3-methyl-1-butene.**

PROBLEM! **Draw the condensed structural formula and the bond-line structure of 2-methylpent-2-ene.**

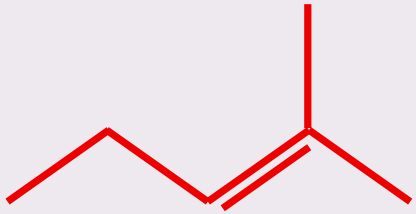
SOLUTION: 1. Draw down the condensed structural formula of the straight chain alkene with 5 carbon atoms with 1 double bond between the second and the third carbon atoms.



2. Replace the hydrogen atom bonded to the second C atom by a methyl group.



3. Draw the bond-line structure:



CAN YOU ANSWER THESE QUESTIONS ?

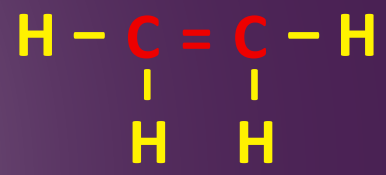
1. What are alkenes?
2. Why are alkenes unsaturated hydrocarbons?
3. How are formed the names of the n-alkenes?
4. What is the molecular formula of decene (alkene with 10 C atoms)?
5. Why do alkenes have chain and position isomers?
6. Why is the alkene name 1-methylprop-1-ene wrong? What is the correct name?
7. Do you expect that alkenes are more reactive than alkanes? Why?

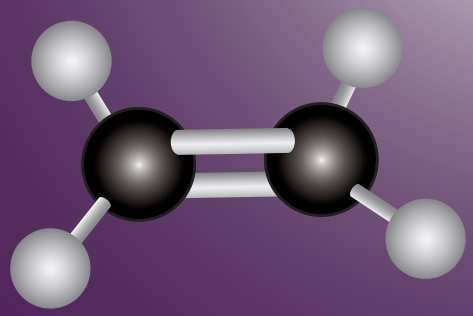
29 Ethene

KEY TOPICS

1. Is ethene a reactive compound?
2. Why addition reactions are typical for ethene?
3. What is a reaction of polymerization?
4. Is ethene a worldwide produced compound?

C_2H_4





KEY WORDS

- Ethene
- Addition reaction
- Hydrogenation
- Halogenation
- Hydration
- Polymerization
- Polymer

ETHENE is the simplest alkene. In its molecules the two carbon atoms are double bonded. Each carbon atom is also covalently bonded to two hydrogen atoms.

$H_2C = CH_2$



PHYSICAL PROPERTIES

At standard conditions ethene is a colourless, flammable gas with a slight odour. Its melting point is -169 °C (higher than ethane) and its boiling point is -105 °C (lower than ethane).

CHEMICAL PROPERTIES

Ethene is more reactive than ethane as one of the shared electron pairs of the double carbon-carbon bond can be easily broken down. These two single electrons can form electron pairs with the valence electrons of other atoms. Thus atoms or atomic groups of some simple substances or compounds (H_2, Cl_2, Br_2, H_2O, HCl etc.) are added to the ethene molecule and ethane or its derivatives are obtained. Such reactions are **addition reactions**.

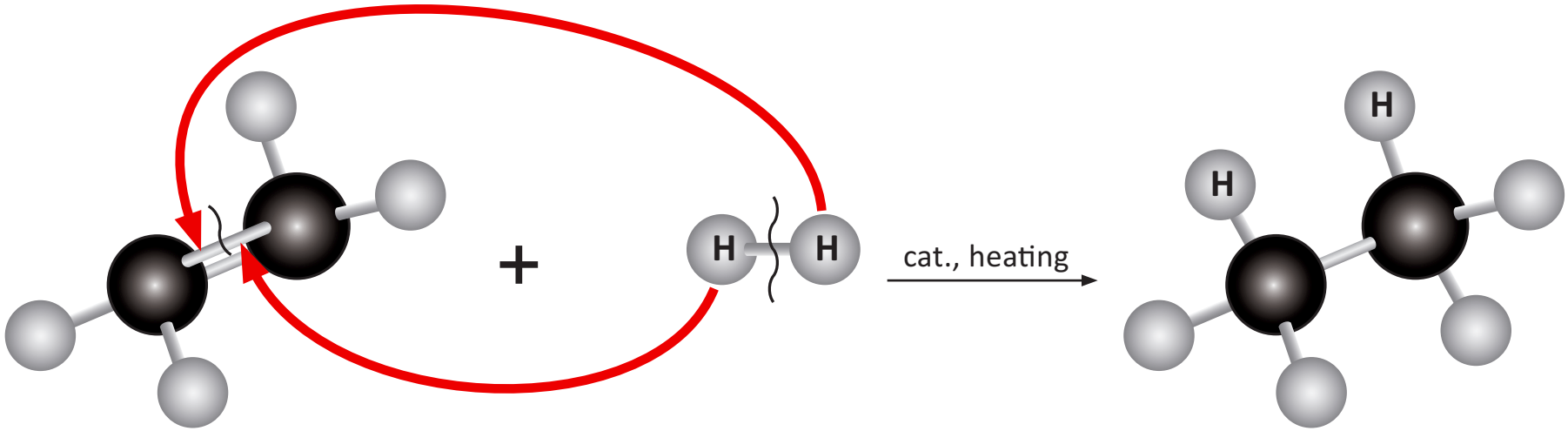
ADDITION REACTIONS ARE CHEMICAL REACTIONS IN WHICH TWO OR MORE DIFFERENT MOLECULES COMBINE TO FORM THE MOLECULE OF A NEW COMPOUND.

Addition reactions occur only if at least one of the reacting molecules has multiple bonds.

Addition reactions are typical for ethene:

HYDROGENATION (addition of hydrogen)

The reaction undergoes in the presence of a catalyst* (Ni, Pt, Pd) and under heating. The H – H covalent bond of the hydrogen molecule and one of the bonds of the carbon-carbon double bond in the ethene molecule break down. The hydrogen atoms bond to the carbon atoms and ethane is produced:



C_2H_4 + H_2 $\xrightarrow{\text{cat., heating}}$ C_2H_6

ethene ethane

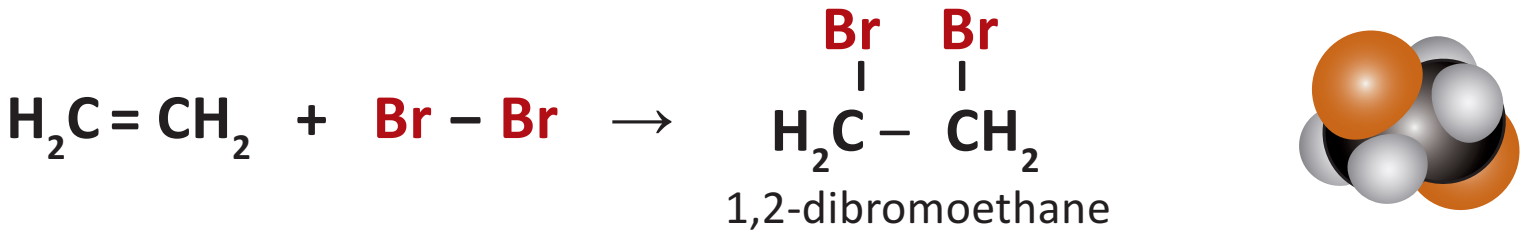
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*Catalysts are substances that accelerate chemical reactions without themselves being consumed.

HALOGENATION (addition of halogens)

Ethene reacts vigorously with fluorine. The addition of Cl_2 and Br_2 is fast enough even at room temperature, while the addition of iodine is much slower.

If ethene bubbles through bromine water, the orange-yellow solution discolours as bromine is added to the ethene, yielding 1,2-dibromoethane:



1,2-dibromoethane

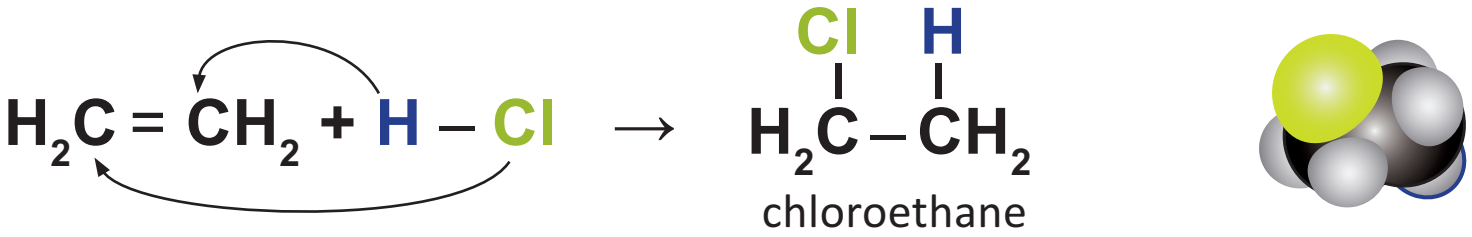
ALL ALKENES TURN THE BROMINE WATER COLOURLESS.
THE DISCOLORATION OF BROMINE WATER IS A TEST REACTION FOR ALKENES.

ANOTHER TEST REACTION FOR ALKENES IS THE DISCOLORATION OF THE PURPLE WATER SOLUTION OF $KMnO_4$ (POTASSIUM PERMANGANATE).

BOTH REACTIONS ARE TEST REACTIONS FOR ALL UNSATURATED HYDROCARBONS.

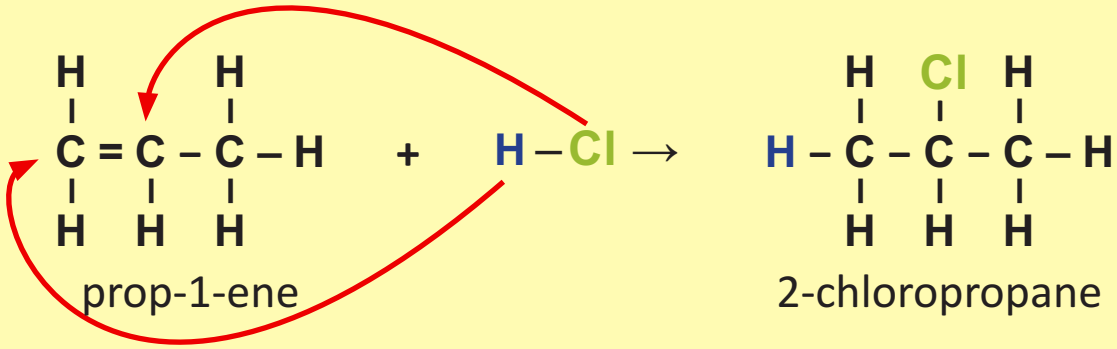
ADDITION OF HYDROGEN HALIDES

The products are halogenoalkanes (alkyl halides). For example:



It is interesting to know:

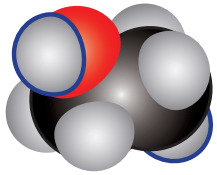
If a hydrogen halide is added to the molecule of an asymmetric alkene (the atoms on both sides of the double bond are not the same, for example propene $CH_2 = CH - CH_3$), the hydrogen atom is added to the carbon atom bonded to the greatest number of H atoms and the halogen atom – to the carbon atom that has the fewest number of H atoms. This is the empirical Markovnikov's rule. For example:



HYDRATION (addition of water)

The reaction undergoes in the presence of a catalyst (H^+ ions). The product is ethanol (an alcohol):

$$H_2C = CH_2 + H - OH \xrightarrow{H^+} \underset{\text{ethanol}}{H_2C(H)-CH_2(OH)}$$



POLYMERIZATION

In Latin „polymerization“ means building up of many parts – under specific conditions (catalysts, heating, high pressure) many (thousands, even millions) molecules bond to each other owing to the breaking of one of the bonds of the double bonded C atoms. A giant macromolecule is formed. The new high molecular weight compound is a polymer. If ethene polymerizes the polymer is *polyethene* (or *polyethylene*):

$$\underset{(n \text{ ethene molecules})}{nH_2C = CH_2} \xrightarrow{\text{polymerization}} \underset{\substack{\text{(a giant polymer macromolecule)}\\ \text{polyethene}}}{-CH_2-CH_2-CH_2-\ldots\ldots-CH_2-CH_2-CH_2-}$$

This polymer is used for the production of one of the most widely used plastics also known as polyethylene.

As all hydrocarbons ethene burns yielding carbon dioxide and water:

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O + \text{heat}$$

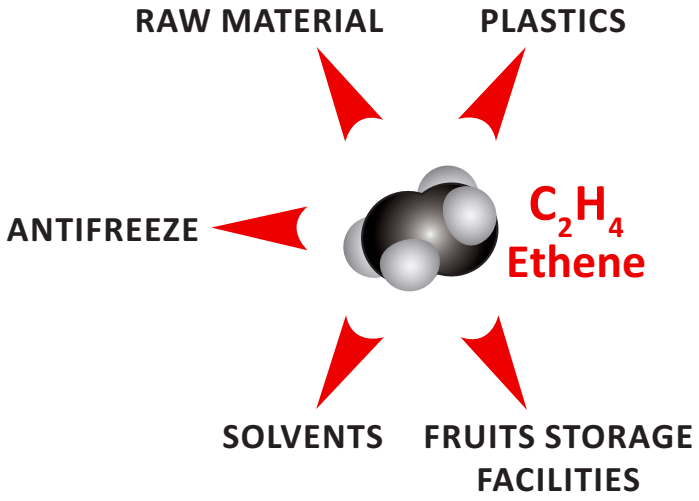
Mixed with air ethene can explode.

PRODUCTION

Ethene is encountered in nature but owing to the increasing demands, millions of tonnes of this alkene are produced every year in the petrochemical industry. Today there is no other organic compound whose industrial production exceeds that of ethene.

USES

Ethene is a raw material for the organic synthesis. Plastics, solvents, the antifreeze and many others are produced using ethene. It is also used to accelerate the ripening of fruits.



CAN YOU ANSWER THESE QUESTIONS ?

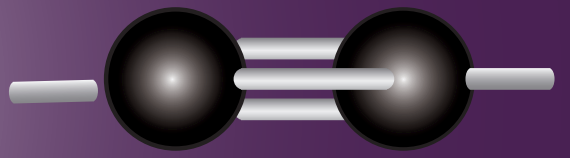
1. Is ethene a saturated or an unsaturated hydrocarbon?
2. Why is ethene more reactive than ethane?
3. What is an addition reaction?
4. Why is the chlorination of ethene an addition reaction?
5. What test reactions for alkenes do you know?
6. What is polyethene?
7. Does ethene burn?

30 Alkynes. Ethyne

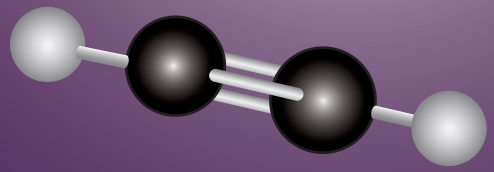
KEY TOPICS

1. What are alkynes?
2. What is the simplest alkyne?
3. Is ethyne a reactive compound?
4. Why is ethyne used to cut and weld metals?

C_nH_{2n-2}



C_2H_2

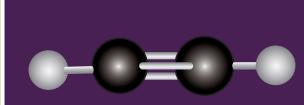
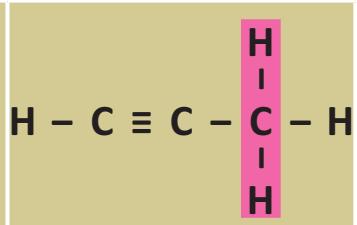
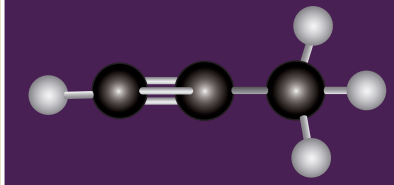
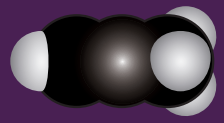


$H-C\equiv C-H$

KEY WORDS

- Alkynes
- Triple bonded carbon atoms
- Ethyne (acetylene)
- Trimerization

ALKYNES are unsaturated hydrocarbons with a triple carbon-carbon bond **– C ≡ C –** in their molecules. As alkanes and alkenes, the straight chain alkynes form a homologous series with the general formula C_nH_{2n-2}. The simplest alkyne is ethyne C_2H_2 (known as acetylene). The next homologue is propyne C_3H_4:

NAME	Molecular formula	Structural formula	Condensed formula	MODEL ball-and-stick	space-filling	bond-line
ETHYNE	C_2H_2	H – C ≡ C – H	HC ≡ CH			
PROPYNE	C_3H_4		HC ≡ C – CH_3			

NAMES AND ISOMERS OF ALKYNES

The names of the straight chain alkynes differ from the names of the straight chain alkanes with the same number of C atoms only in the suffix – „-ane“ is replaced by „-yne“. The C atoms are numerated in such a way as to assign to the triple bonded C atoms the lowest possible numbers. The number of the first triple bonded C atom is written, separated by dashes, before the suffix (or before the name).

C_2H_2	ethyne
C_3H_4	propyne
C_4H_6	butyne
C_5H_8	penyne
C_6H_{10}	hexyne

$HC \equiv C - CH_2 - CH_2 - CH_3$

pent-1-yne or 1-pentyne

$HC \equiv C - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_3$

3-methylbut-1-yne
or 3-methyl-1-butyne

Chain isomers
of pentyne C_5H_8

Alkynes with more than 4 C atoms have chain and position isomers. The carbon skeleton may be straight or branched and different adjacent C atoms may be triple bonded. The naming of the alkynes isomers follows the same rules as for the alkenes, but the suffix „-ene“ is replaced by the suffix „-yne“.

$\overset{1}{HC} \equiv \overset{2}{C} - \overset{3}{CH_2} - \overset{4}{CH_3}$

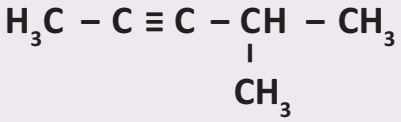
but-1-yne
or 1-butyne

$\overset{1}{H_3C} - \overset{2}{C} \equiv \overset{3}{C} - \overset{4}{CH_3}$

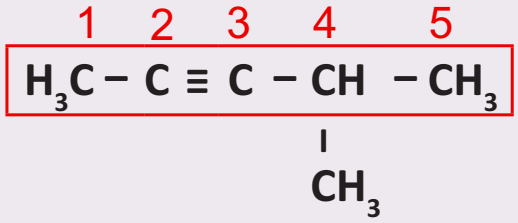
but-2-yne
or 2-butyne

Position isomers
of butyne C_4H_6

PROBLEM! **Name the alkyne:**



SOLUTION: 1. The longest chain with the triple carbon-carbon bond is composed of 5 C atoms. The second and the third C atoms are double bonded. So this alkyne is a branched pent-2-yne (or 2-pentyne):



2. The branch is a methyl group bonded to the fourth C atom. So the name of the branch is 4-methyl.

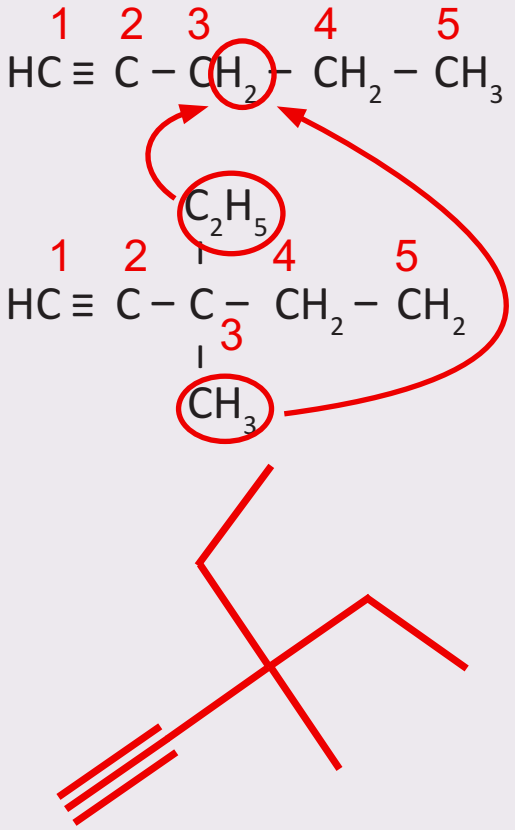
ANSWER: The name of the alkyne is **4-methylpent-2-yne** or **4-methyl-2-pentyne.**

PROBLEM! **Draw the condensed structural formula and the bond-line structure of 3-ethyl-3-methylpent-1-yne.**

SOLUTION: 1. Draw down the condensed formula of the straight chain alkyne with 5 carbon atoms with a triple bond between the first and the second C atoms:

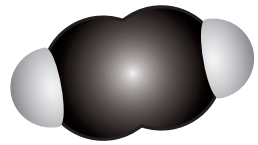
2. Replace the hydrogen atoms, bonded to the third C atom by an ethyl group and a methyl group:

3. Draw the bond-line structure:



ETHYNE

$HC \equiv CH$



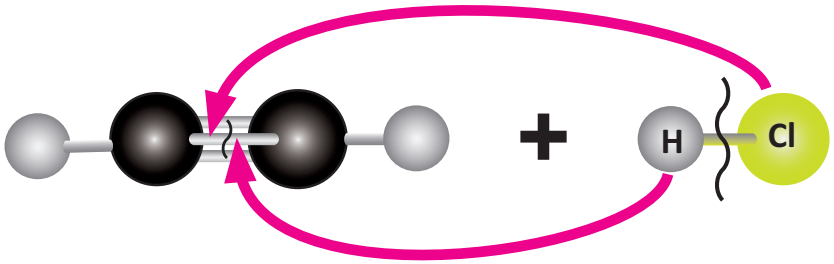
Pure ethyne (also known as acetylene) is a colourless and almost odourless gas (at standard pressure and at temperatures higher than –84 °C). Its unpleasant odour is caused by some impurities.

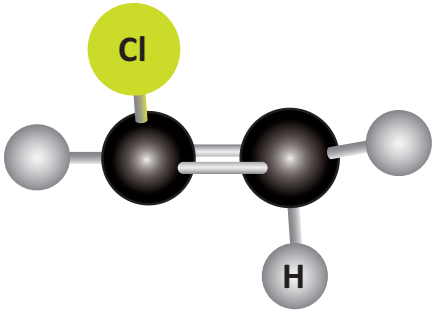
CHEMICAL PROPERTIES

Ethyne is a reactive compound as one or two of the bonds between the triple bonded C atoms can be broken down – addition reactions easily take place. Substitution reactions also occur as one or both carbon-hydrogen covalent bonds can break down too.

ADDITION REACTIONS

- Molecules of hydrogen, halogens, hydrogen halides are easily added to the ethyne molecule. First, one bond breaks down and ethene or its halogen derivatives, are obtained. The next stage of the reaction is the breaking down of the second bond and the addition of a second molecule. For example the addition of hydrogen chloride HCl undergoes in two stages – first C_2H_3Cl (chloroethene) is produced. In the second stage one more molecule of HCl is added and 1,1-dichloroethane is produced (Explain why the main product of the reaction is 1,1-dichloroethane, rather than 1,2-dichloroethane. Remember the Markovnikov's rule.):

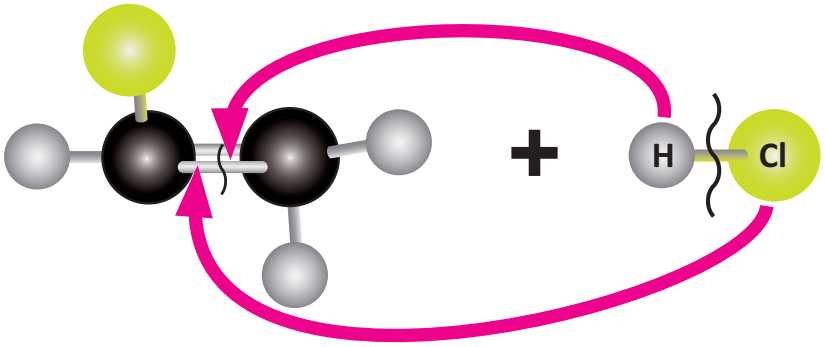


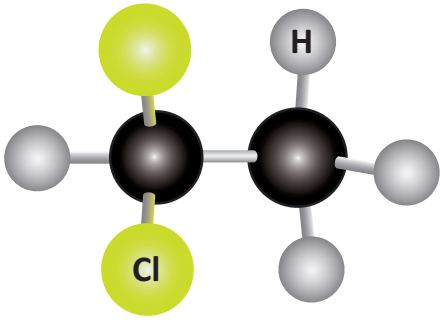


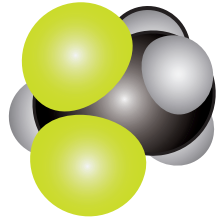
$HC{\equiv}CH + H{-}Cl \longrightarrow Cl{-}CH{=}CH_2$

ethyne

chloroethene (vinyl chloride)





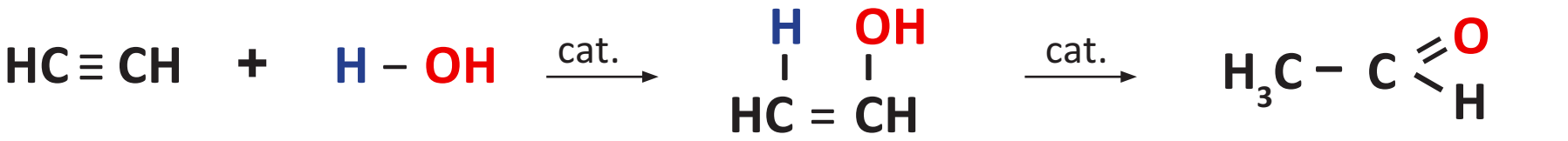


$Cl{-}CH{=}CH_2 + H{-}Cl \longrightarrow Cl{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}CH_3$

1,1-dichloroethane

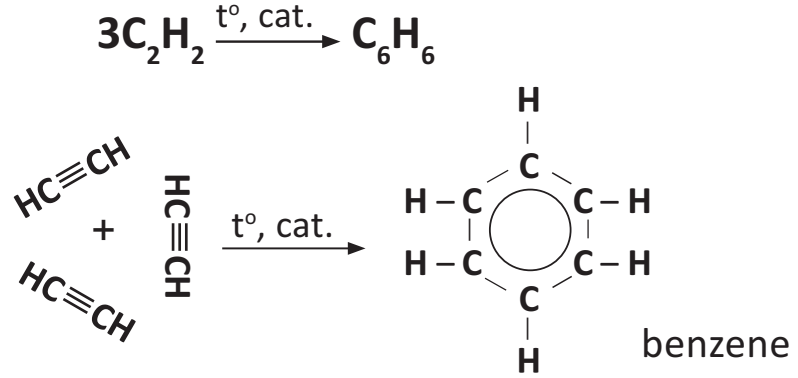
The discoloration of bromine water and a solution of $KMnO_4$ are test reactions for ethyne.

- Ethyne adds water too, but the mechanism of this reaction is a little bit more complicated. The product in the first stage is ethenol (an unsaturated alcohol). It is unstable and the next stage of the reaction is the catalytic rearrangement of the atoms in the molecule – the final product is named ethanal (you will become familiar with this compound later in this course). This specific reaction is known as the Kucherov's reaction (in the name of the scientist who discovered it):



ethenol **ethanal (acetaldehyde)**

- The *bonding of three ethyne molecules* under heating and in the presence of a specific catalyst, is called trimerization. The molecules bond to each other forming a ring. The name of the new compound is benzene C_6H_6 (the simplest aromatic hydrocarbon):



It is interesting to know::

SUBSTITUTION REACTIONS

One or both H atoms in the ethyne molecule can be substituted by atoms of some metals (Na, K, Ca and others). The products are salts – *ethynides* (if only 1 H atom is substituted) and *carbides* (both H atoms are substituted):

$$2HC \equiv CH + 2Na \rightarrow \underset{\text{sodium ethynide}}{2NaC \equiv CH} + H_2\uparrow$$

$$HC \equiv CH + Ca \rightarrow \underset{\text{calcium carbide}}{Ca\begin{matrix}C\\ \vdots\\ C\end{matrix}} + H_2\uparrow$$

This type of reactions is essential for the organic synthesis as the products are *organometallic* compounds which are often used as catalysts or specific reagents.

COMBUSTION

In the air ethyne burns with a smoky flame. In pure oxygen the flame is not smoky and the temperature rises to about 3000 °C. For this reason ethyne is used for fuelling the acetylene torch (burner) used to cut or weld metals. The products of the ethyne combustion are carbon dioxide CO_2 and water H_2O.

The mixture of ethyne and air is explosive. Sparks or flame may cause it to explode violently. At a high pressure the volume of the gas shrinks and the ethyne can explode too – it decomposes into hydrogen and carbon and a considerable amount of heat is liberated. Therefore the safety recommendations when working with ethyne must be always strictly respected.

PRODUCTION

Ethyne is of major importance for the industry. It is a product of the oil processing.

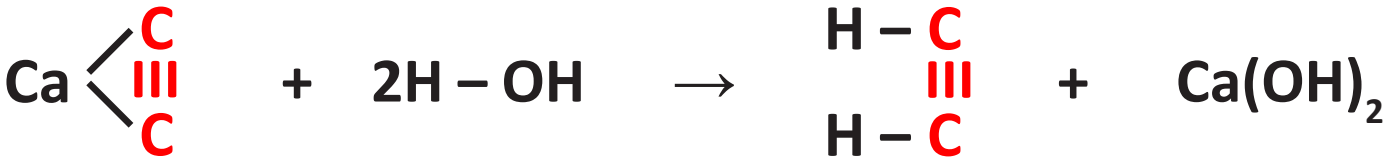
It is also produced from methane or in a direct synthesis from its elements – carbon and hydrogen. At a relatively high temperature (about 1500 °C) methane transforms into ethyne:

$$2CH_4 \rightarrow C_2H_2 + 3H_2$$

The direct synthesis from carbon and hydrogen is carried out in an electrical arc (at thousands of degrees Celsius):

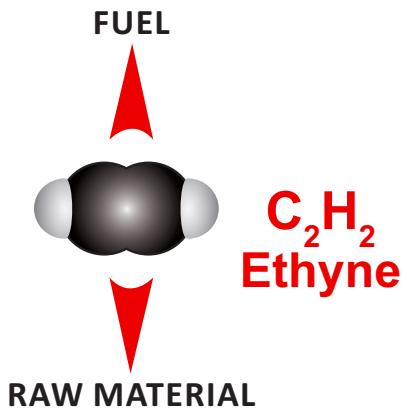
$$2C + H_2 \rightarrow C_2H_2$$

In the laboratory ethyne can be prepared from calcium carbide in a vigorous reaction with water:



USES

Ethyne is a fuel with a high flame temperature. It is also used as a raw material in the synthesis of organic compounds (benzene, acetaldehyde, chloroprene, vinyl chloride, acetic acid, etc.).



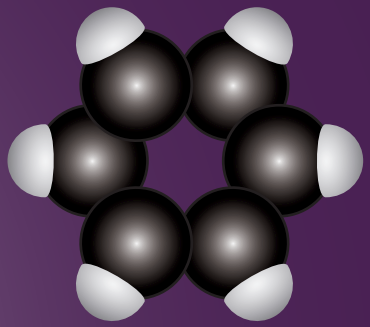
CAN YOU ANSWER THESE QUESTIONS ?

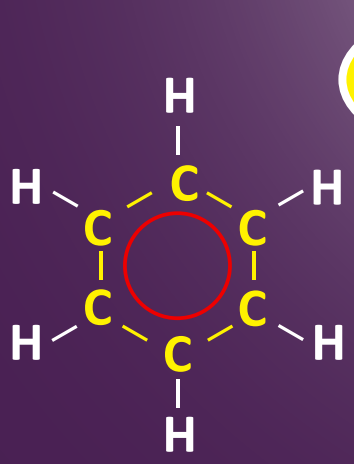
1. What are alkynes?
2. Why are alkynes unsaturated hydrocarbons?
3. How many hydrogen atoms are there in a molecule of heptyne?
4. Do alkynes have isomers?
5. What is the simplest alkyne?
6. Does butyne have chain isomers?
7. Why is ethyne used to weld and cut metals rather than methane or natural gas?
8. Why is ethyne stored in gas cylinders dissolved in appropriate solvents?

31 Arenes. Benzene

KEY TOPICS

1. What are arenes?
2. Why is the benzene molecule planar?
3. What is an aromatic character?
4. Is benzene harmful for man and environment?





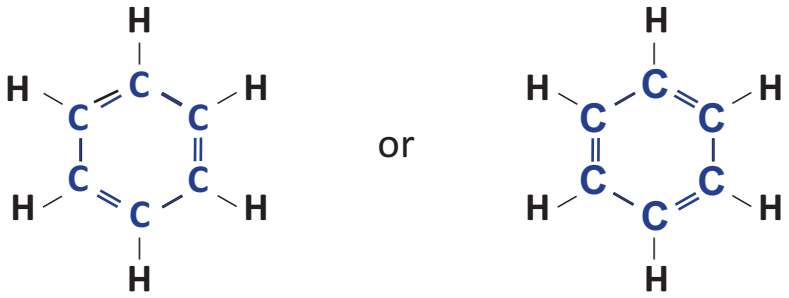
C_6H_6



KEY WORDS

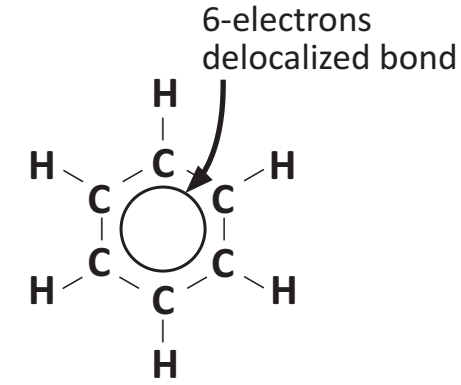
- Arenes
- Aromatic hydrocarbons
- Delocalized bond
- Aromatic character
- Halogenation
- Chlorination

ARENES are a major class of organic compounds. They are also known as aromatic hydrocarbons as the first discovered arenes had a pleasant smell. Most of arenes do not smell nice but in spite of that this trivial name is commonly used.

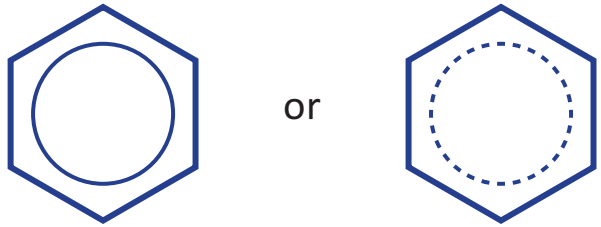


KEKULE'S STRUCTURAL FORMULA OF BENZENE C_6H_6

All arenes have in their molecules a 6-carbon atoms ring. The simplest arene is benzene $\mathbf{C_6H_6}$. In the second half of the XIXth century August Kekule was the first to suggest that the six C atoms in the benzene molecule form a ring with alternating single and double carbon-carbon bonds. Later it was proved that the adjacent carbon atoms share only one electron pair and six single electrons (one from each C atom) form a specific delolacalized bond. This bond can not be represented in a Lewis structure – the single electrons are not anymore attached to a specific C atom and move around the nuclei of all six C atoms. With the fourth single electron each C atom forms a single covalent bond with one hydrogen atom. As a whole, the molecule of benzene is planar (a regular hexagon).

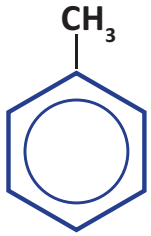


MODERN STRUCTURAL FORMULA OF BENZENE C_6H_6

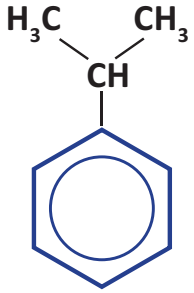


BOND-LINE STRUCTURE OF BENZENE C_6H_6

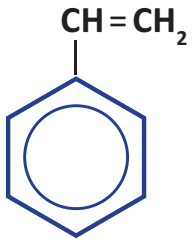
Arenes are derivatives of benzene – one or more hydrogen atoms in its molecule are substituted by hydrocarbons groups (contain one H atom less than the hydrocarbons). For example:



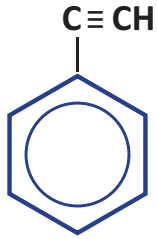
Methylbenzene
(toluene)



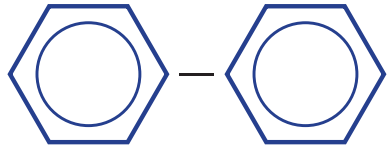
Isopropylbenzene



Ethenylbenzene
(styrene)

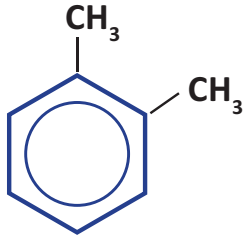


Etynylbenzene

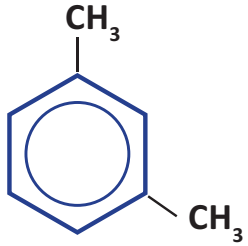


Biphenyl

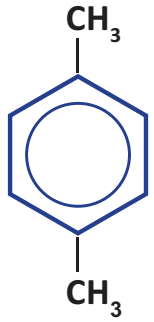
Benzene derivatives have position isomers if two or more H atoms are substituted with hydrocarbons groups. Their properties depend on the position of these hydrocarbon groups. For example dimetyl-benzene $C_6H_4(CH_3)_2$ has three isomers:



1,2-dimetylbenzene
(*o-xylene)

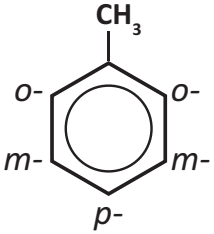


1,3-dimetylbenzene
(*m-xylene)

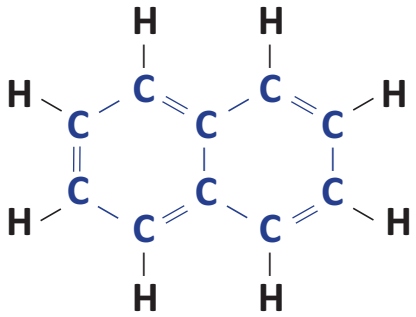


1,4-dimetylbenzene
(*p-xylene)

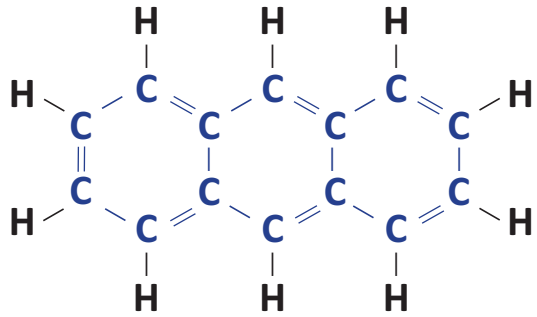
*The place of the substituents is indicated by the symbols: *o*- (abbreviation of „ortho“), *m*-(abbreviation of „meta“) and *p*- (abbreviation of „para“):



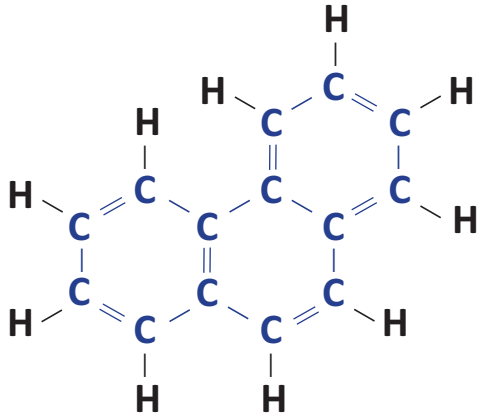
The polycyclic arenes (known as PAHs – abbreviation from **P**olycyclic **A**romatic **H**ydrocarbons) are composed of two or more joined aromatic rings (two C atoms are common for adjacent rings). The simplest PAH is naphthalene:



Naphthalene

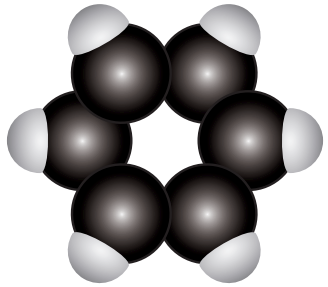


Anthracene



Phenanthrene

BENZENE



Benzene was isolated by Michael Faraday in the first half of the XIXth century.

He established its composition – C_6H_6.

PHYSICAL PROPERTIES

At STP benzene is a volatile liquid – it melts at 5,5 °C and boils at 80,1 °C. Its density is 880 kg/m^3 and practically it is insoluble in water. So it flows over the water. It is soluble in some organic solvents. Benzene is a flammable liquid with a specific odour.

! Benzene is a toxic compound. It is considered as a class A carcinogen. It can be inhaled or absorbed through the skin. It may have a narcotic effect. Benzene is a serious pollutant of soils and water.

CHEMICAL PROPERTIES

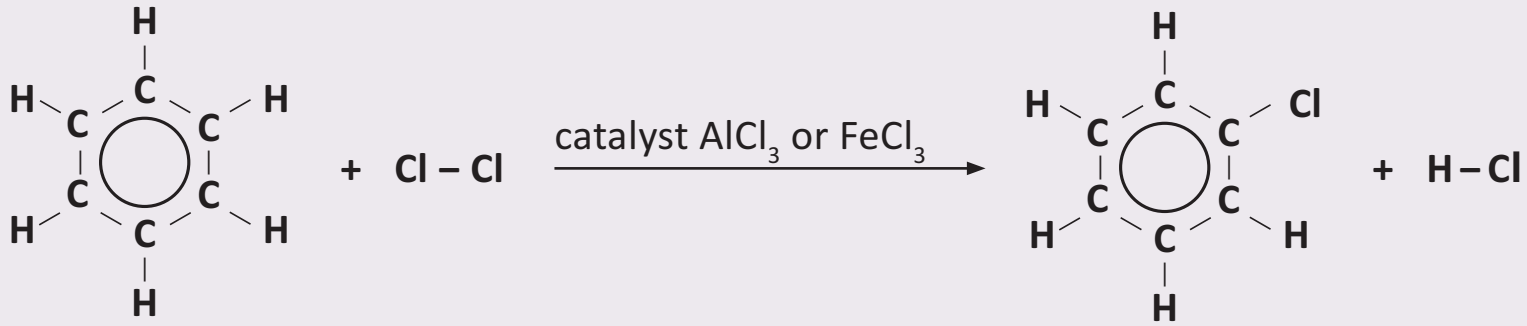
The 6-atoms ring of benzene is a stable structure. It is difficult to break down the delocalized bond. Therefore the substitution of one or more H atoms by other atoms or atomic groups are the most common reactions of benzene. These reactions undergo easily as compared to alkanes and are essential for the so called aromatic character of benzene:

HALOGENATION

The reaction is catalytic*. $AlCl_3$ or the corresponding iron trihalogenide (for example $FeCl_3$ for the process of chlorination) is used. The product is a halogenobenzene.

PROBLEM! **Express the chemical equation of the chlorination of benzene. Use structural formulae and name the products.**

SOLUTION: The chemical equation of the reaction is:

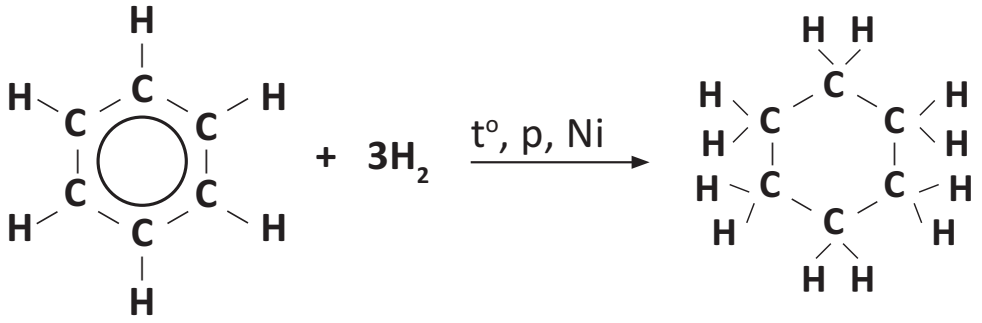


ANSWER: The name of the products are **chlorobenzene** and hydrogen chloride.

*Catalytic reactions undergo only in the presence of catalysts – substances that accelerate chemical transformations without themselves being consumed.

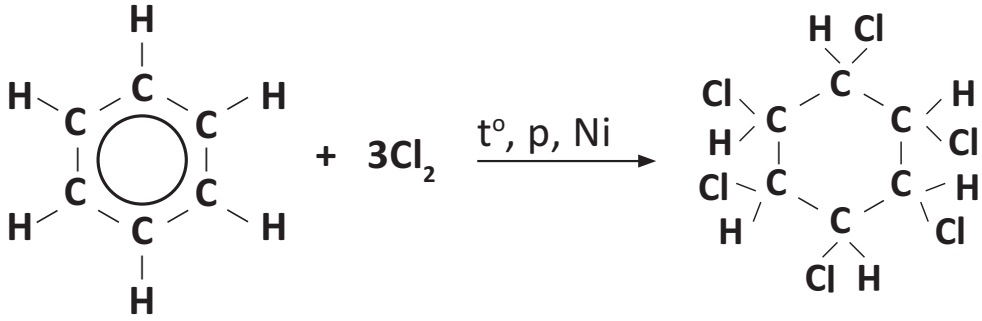
ADDITION REACTIONS

Under special conditions benzene takes part also in addition reactions. Under high pressure and heating and in the presence of a catalyst (Ni), three molecules of hydrogen are added to the benzene molecule yielding one molecule of cyclohexane C_6H_{12}:



cyclohexane

Exposed to light benzene reacts with chlorine to produce 1,2,3,4,5,6-hexachlorocyclohexane $C_6H_6Cl_6$. It is known as preparation 666 and is an insecticide:



1,2,3,4,5,6-hexachlorocyclohexane

PRODUCTION

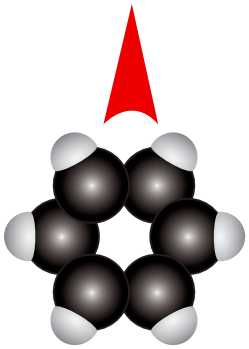
Benzene and its derivatives are products of the oil processing industry. Benzene is also synthesized in the reaction of trimerisation of ethyne (see p. 58) and can be prepared also from cyclohexane. This is the reverse reaction of the process of hydrogenation of benzene. The reaction is catalytic and undergoes at high temperature:

$$C_6H_{12} \xrightarrow{\text{cat., heating}} C_6H_6 + 3H_2\uparrow$$

USES

Benzene is mainly used as a row material in the organic synthesis. The methylbenzene (toluene or toluol) $C_6H_5CH_3$ is a good solvent of many organic compounds and is also used in the pharmaceutical industry, in the production of dyes, explosives and others. The dimethylbenzene (xylene or xylol) $C_6H_4(CH_3)_2$ is a solvent of varnishes and dyes and is also a raw material for the organic synthesis. From ethenylbenzene $C_6H_5CH{=}CH_2$ (vinylbenzene, phenylethene, styrene or styrol) is produced the polymer polystyrene, main component of one of the most widely used plastic.

RAW MATERIAL



C_6H_6
Benzene

CAN YOU ANSWER THESE QUESTIONS ?

1. What is the difference between unsaturated and aromatic hydrocarbons?
2. Why is benzene an aromatic hydrocarbon?
3. What is the shape of the benzene molecule?
4. Why is benzene not used today as a solvent?
5. Why do substitution reactions of benzene undergo easily as compared to alkanes?
6. Why is it possible to add hydrogen or chlorine atoms to the benzene molecule?
7. How many moles of CO_2 are evolved in the combustion of 1 mole of benzene?

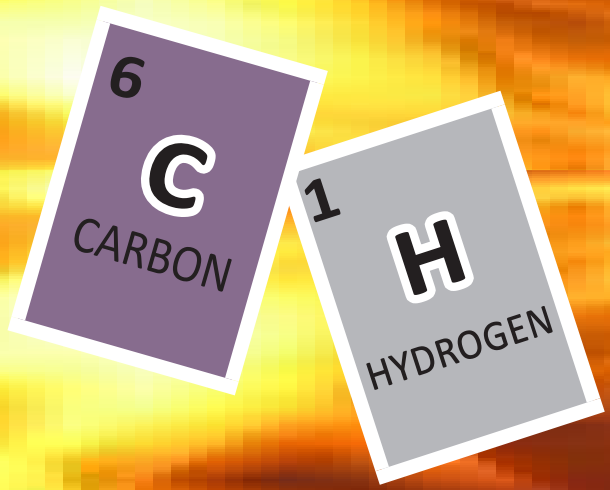
32 NATURAL SOURCES OF HYDROCARBONS

KEY TOPICS

1. What are the main natural sources of hydrocarbons?
2. Why is the crude oil processed?
3. Why are oil fractions submitted to a secondary refining?
4. Why are oil spills disastrous for the environment?

KEY WORDS

- Natural gas
- Crude oil
- Coal
- Refinery
- Fractional distillation
- Fractionating column
- Cracking
- Reforming



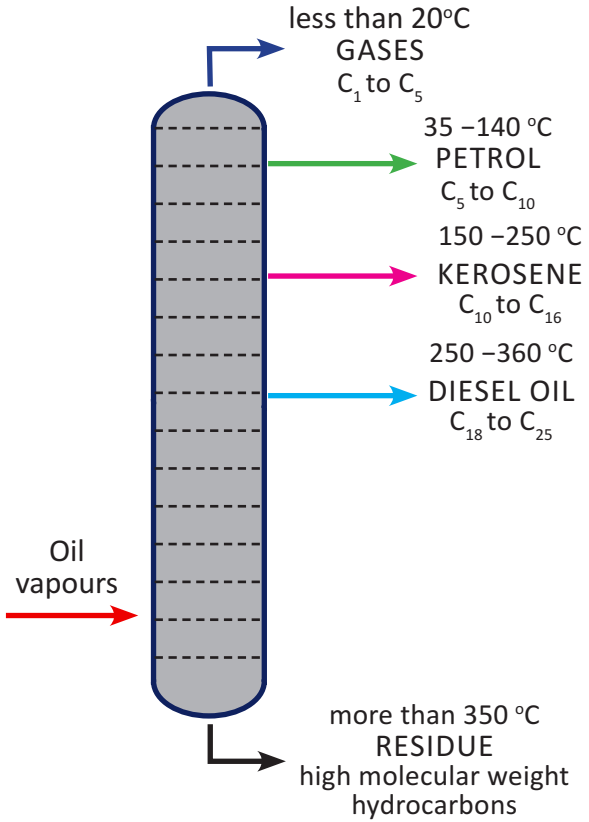
The most important natural sources of hydrocarbons are natural gas, crude oil and coal.

NATURAL GAS is a fossil fuel and is a nonrenewable resource. It contains mainly methane, but also ethane, propane, butane, ethene, ethyne, nitrogen, carbon dioxide, hydrogen, dihydrogen sulfide, argon, helium and other gases in much smaller quantities. It is a cheep fuel with high calorific values – about 35 000 kJ/m^3 (depend on the gas composition and are different for the different gas fields). The petroleum gas (a mixture consisting mainly of gaseous hydrocarbons) is found in nature in the petroleum fields. Either it forms a gaseous layer above the crude oil, or it is dissolved in it. The calorific values of petroleum gas are high as compared to the natural gas.

CRUDE OIL is a heavy dark brown oily liquid. It is insoluble in water and with a specific odour. Crude oils from different oil-producing area have different compositions, but mainly contain aliphatic (saturated, unsaturated, cyclic) hydrocarbons, aromatic hydrocarbons and in small quantities compounds of nitrogen, oxygen, sulfur and others.

Crude oil is processed in *petroleum refineries*. The first step is the separation of water, dissolved salts and rocks . Next, in a complex process, different oil fractions, consisting of hydrocarbons with similar properties and narrow differences in boiling points, are separated – that is the oil fractional distillation. This is a physical process based on the difference in the boiling temperatures of hydrocarbons with different molecular weights. Oil is heated to about 350 °C and the hydrocarbon vapours are piped into a high column (fractionating column). The vapours rise in the column and cool. When the boiling temperature of a component of the vapours is reached, it condenses and the liquid is collected. At different heights of the column different fractions of hydrocarbons are removed.

*Calorific value is the quantity of heat produced by the complete combustion of a given mass of fuel, usually expressed in joules per kilogram.



FRACTIONATING COLUMN

The fractions of the low molecular weight hydrocarbons are collected at the top of the column as their boiling points are the lowest. In contrary – at the bottom are collected the fractions of the heaviest hydrocarbons. Fractionating columns are vertical cylinders with heights ranging from a few meters to 100 and even more meters.

PETROL is a mixture of hydrocarbons with 5 to 10 or 12 carbon atoms. It is a fuel (also known as gasoline in North America) for the internal combustion engines. Also it is a good solvent. High quality petrol is volatile, with high calorific values and must be resistant to detonation (the auto-ignition of the vapour-air mixture in the engines). The octane number (or rating) of a fuel is a measure of its capability to resist to detonation. In general, branched hydrocarbons are more resistant than straight chain hydrocarbons. The most resistant is 2,2,4-trimethylpentane (i-octane). Its octane number is 100. The octane number of n-heptane is assumed to be 0 as it is not resistant to detonation at all. The petrol octane number denotes the percentage (by volume) of i-octane in a mixture, containing i-octane and n-heptane, which detonation characteristics match those of the tested petrol. Petrol with octane number 84 detonates as a mixture of 84 % of i-octane and 16 % of n-heptane. The higher is the octane number, the slower and more uniform is the fuel combustion. Octane numbers are determined experimentally.

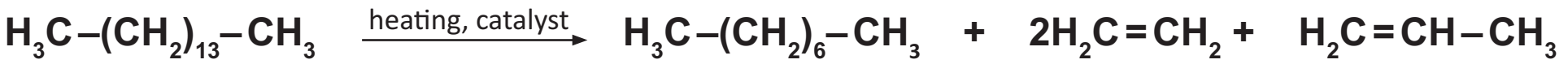
KEROSENE (also known as lamp oil) and DIESEL OIL are also used as engine fuels. Kerosene, after being specially treated, is used as a jet fuel.

The RESIDUE is treated at low pressure to be separated in fractions by the so called vacuum fractional distillation (At high temperatures high molecular weight hydrocarbons decompose. The process undergoes at low pressures as the boiling temperatures of the compounds decrease). The products are *paraffin waxes* and *bitumen*.

CRACKING and REFORMING

The oil fractions are submitted to further refining as the long chain hydrocarbons are not so useful as fuels or for industry purposes as the short chain fractions (for example petrol or kerosene). The heavy hydrocarbons (with high molecular weights) can split (crack) – their carbon chains are broken down and light hydrocarbons are produced. The process is called cracking. The reactions are catalytic and undergo at high temperatures. The product is a mixture of lower molecular weight saturated and unsaturated hydrocarbons:

LONG CHAIN ALKANE $\xrightarrow{\text{heating, catalyst}}$ **SHORT CHAIN ALKANE + ALKENES**



pentadecane — n-octane — ethene — propene

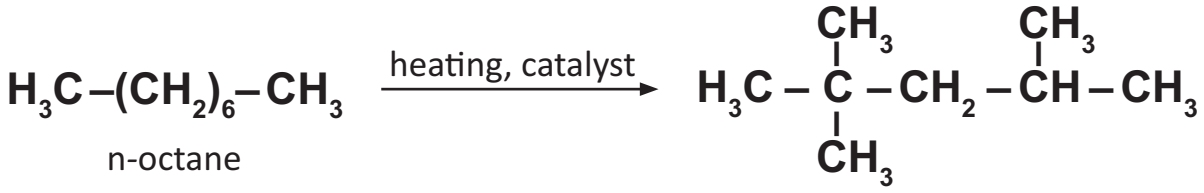
The cracking process is followed by a distillation process to separate the components of the mixture – octane is a component of petrol, while ethene and propene are row materials for plastic manufacturing.

The straight chain alkanes have low octane numbers and are low grade fuels. To convert them to high grade fuels the structure of their carbon chains must be „reformed“ – branching or cycling of the carbon chains must occur. This industrial process is carried out under special conditions (high temperature and pressure, catalyst) and is called reforming*:*

STRIGHT CHAIN ALKANE —(heating, catalyst)→ **BRANCHED CHAIN ALKANE**

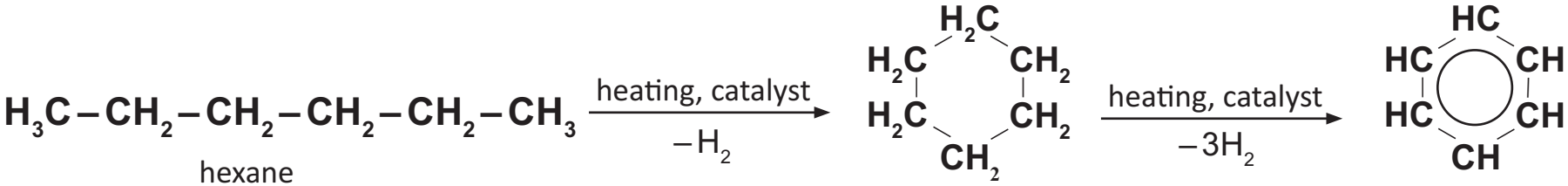
STRIGHT CHAIN ALKANE —(heating, catalyst)→ **CYCLOALKANE**

For example in a reforming processes n-octane isomerises to give 2,2,4-trimethylpentane and hexane is converted into cyclohexane, which is transformed into benzene:



n-octane

2,2,4-trimethylpentane (i-octane)



hexane

cyclohexane

benzene

Generally, the products of the oil processing are fuels and different compounds for the industry. The most important is ethene. Other basic petrochemicals are propene, butadiene ($H_2C=CH-CH=CH_2$), benzene, methylbenzene (toluene), dimethylbenzene (styrene) and others.

COAL is a solid fossil fuel, but after being specially treated it can become a source of coke, coke gas (mixture of mainly CH_4 and H_2), tar, aromatic hydrocarbons, ammonia and others.

ENVIRONMENTAL ISSUES

Oil, gas or coal processing may cause water, air or soil pollution. The development of wasteless technologies is a key factor for safeguarding the environment.

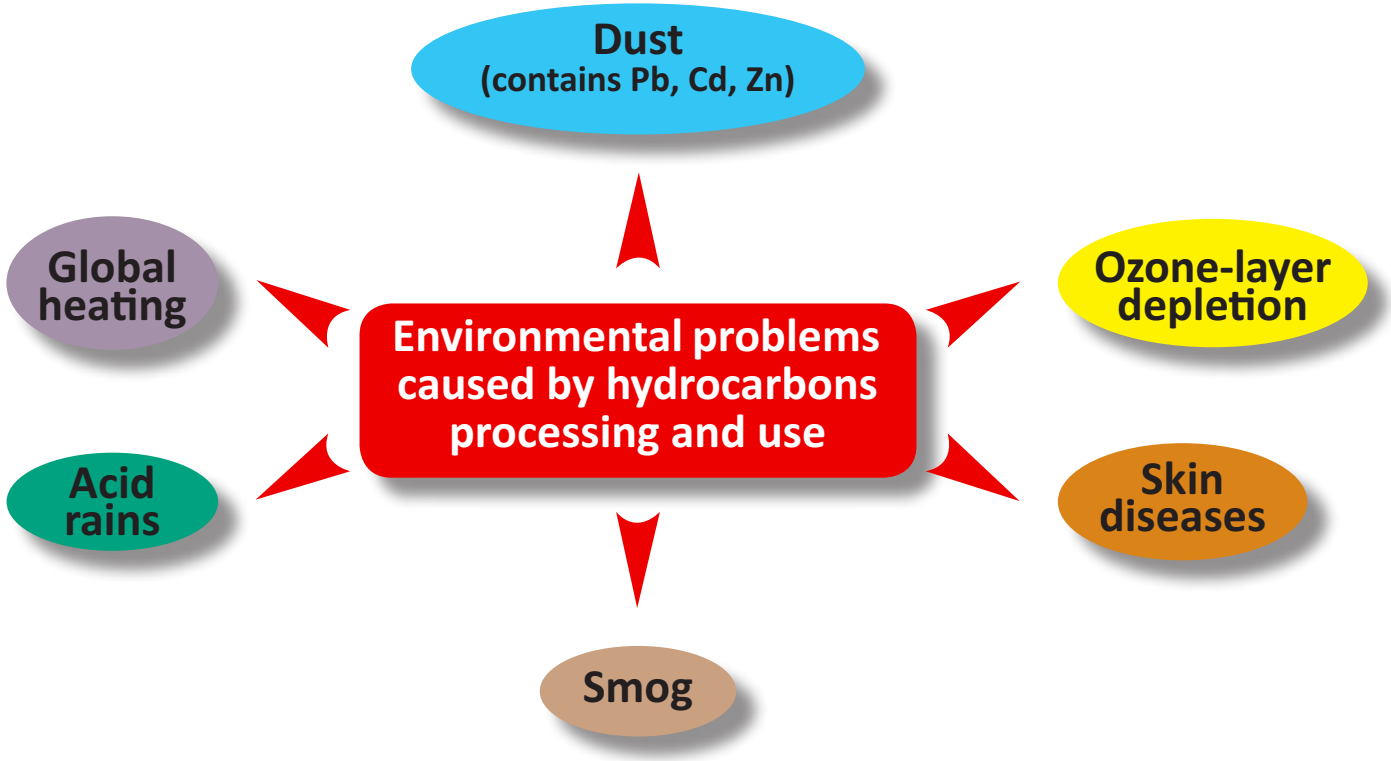
The wide use of fuels dramatically contributes to the accumulation of CO_2 in the atmosphere and consequently to the global warming of the planet. In incomplete combustion besides CO_2, CO may be also released.

Some hydrocarbons and nitrogen dioxide, evolved in the air, react with the oxygen under the action of sunlight. The products (the so called photochemical smog) irritate the eyes and affect the respiratory system.

In the combustion of jet fuels nitrogen oxides, which are ozone-depleting gases, are emitted. Raw natural gas may have sulfur-containing compounds. It is processed to remove the impurities as in combustion sulfur oxides are emitted. Together with nitrogen oxides they come back to the Earth surface as acid rains.

In fuel combustion a fine dust (solid particles with diameter of about 0,002 cm) may be also formed. If inhaled it may be dangerous for the health, because it contains heavy metals as lead, cadmium, zinc and others.

The smog (an atmospheric layer over towns with high content of pollutants – gases with harmful effects, dust) may be dangerous for everyone but is especially harmful for persons with respiratory problems and for the children.



CAN YOU ANSWER THESE QUESTIONS ?

1. What are the main natural sources of hydrocarbons?
2. Why are natural gas, crude oil and coal fossil fuels?
3. Are natural gas, crude oil and coal renewable resources?
4. How is crude oil separated into fractions?
5. Why are oil fractions submitted to reforming and cracking?
6. Why should always be considered the impact on the environment of the fuels combustion?

PROJECTS

1. HOW MANY SUBSTANCES ARE KNOWN TODAY?

Use data of CAS (www.cas.org). Pay attention what substances are registered and how each one of them is identified. How many are the known organic compounds? Does their number grow rapidly?

2. NATURAL GAS

Where are the major gas fields in the World? What is the composition of the natural gas depending on the gas field? What is a calorific value of a fuel and why is it important? Compare the quality of natural gas from different fields.

3. ALKANES IN THE UNIVERSE

Are there scientific data proving the existence of some alkanes (enumerate them) on other planets in the Solar system? Can you give some ideas about their use?

4. THE STRUCTURAL THEORY – A MILESTONE IN THE UNDERSTANDING OF MATTER

Learn more about the basis of the structural theory. Explain why it is so important for the understanding of the properties of compounds.

5. ISOMERISM

Learn when the isomerism has been discovered and what were the first isomers synthesized in the laboratory.

6. ETHENE

Why is ethene the major petrochemical product? What is the annual world production of ethene?

7. THE ACETYLENE BURNER

Familiarise yourself with the construction and the operating principle of the acetylene burner. Pay attention to the safety precautions that must be respected when working with the burner.

8. STRUCTURE OF THE BENZENE MOLECULE

Learn where, when, how and by him has been established the structure of the benzene molecule. Explain why this molecule is stable and how the chemical and physical properties of benzene are affected by the structure of its molecules.

9. THE MAJOR OIL DISASTERS

Learn where and when major oil disasters happened. How had oil spills damaged the environment? How long did the nature recover after the disasters? Was it possible to avoid these disasters?