

Chemistry course
ACME Faculty, EHVE course
B.Sc. Studies, I year, I semester
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Organic chemistry - basics

Chemistry of carbon

- Organic chemistry is chemistry of carbon compounds.
- Other elements, which usually appear in organic compounds, are hydrogen, oxygen, nitrogen, less frequently sulfur, phosphorus and halogens. Rarely, other non-metals and alkali metals appear. If we would take into account all metal complexes with organic compounds, almost every element can be a part of organic compound.

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Chemistry of carbon

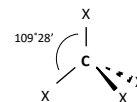
- Carbon is the only element, which is the base for such numerous compounds. It results from its unique electron structure.
- Carbon is in the "middle" of the 2. period and has 4 valence electrons ($2s^2 2p^2$). Thus, it has a large capacity for forming covalent bonds – especially with other carbon atoms. As a result, chemistry of carbon is so rich.
- Covalent bonds are based on stable connection of atoms by mutual sharing of electrons instead of giving them away by one of atoms (that's a dative bond) or electrostatic interactions (ionic bond).

Li Be B C N O F Ne

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Hybridization – sp^3

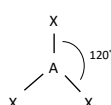
Carbon atom can form four bond maximum (it has four valence electrons). Connected atoms tend to be as far from each other as it is possible – they place themselves in the vertices of a tetrahedron. In that kind of arrangement they are equivalent (assuming all bonds connecting to the same element, carbon for instance), SO there is a hybridization of orbitals. In that case it means it will be sp^3 hybridization, consisting of one s -type orbital and three p -type orbitals (in hybrid form they have less energy than sum of energies of their initial components – $1x s + 3x p$; to achieve such hybrid state excitation of one s electron to p -state is needed; ground state of carbon is $2s^2$ and $2p^2$).



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Hybridization – sp^2

- Result of 1 s and 2 p electrons hybridization is formation of sp^2 hybridization (three orbitals). Energy of each orbital of sp^2 hybrid is a little lower than that of sp^3 orbital. Third p electron unused in hybrid occupies p orbital perpendicular to the plane formed by sp^2 orbitals.



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Hybridization - sp

- Result of 1 s orbital and 1 p orbital hybridization is formation of sp hybrid (two orbitals). Energy of sp orbital is even lower (and more stable) than that of sp^2 (or sp^3).
- sp , sp^2 and sp^3 orbital shapes are alike and looks like an eight rotated in space (sandglass with one very small glass bulb).
- Hybridized orbitals form sigma (σ) bonds with other atoms.



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Double bonds

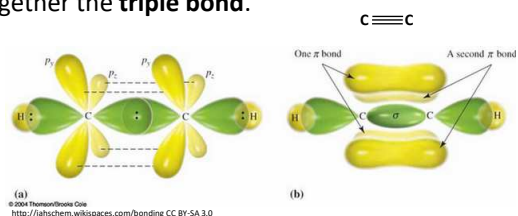
If carbon atoms (or carbon and other atom, so-called heteroatom) with sp^2 hybridization form a bond (σ type) unused p orbitals (perpendicular to the sp^2 – and sigma bond – plane) of both atoms superpose on sides of σ bond forming additional pi (π) bond. One σ bond and one π bond form together **double bond**.



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Triple bonds

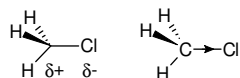
Similarly to double bonds, two carbon atoms (or carbon and heteroatom) with sp hybridization form two additional π bonds made of two p orbitals of each atom that superpose from the side of σ bond. One σ bonds and two π bonds form together the **triple bond**.



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Bonds with elements from the edges of periodic table

Bonds with chlorine or fluorine, due to their high affinity to electrons (higher than carbon one) are “shifted” towards chlorine/fluorine, *i.e.* electron density (chance to find the electron) is higher closer to the halogen. It means, that the **partial negative charge** forms (δ^-) on halogen atom and partial positive charge (δ^+) on carbon. Such bond is called the **polarized bond**.

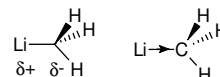


Ways to indicate polarized bond – by showing partial charges or just with an arrow pointing towards more negatively charged atom.

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Bonds with elements from the edges of periodic table

Also carbon-lithium atom would be strongly polarized. In that case the partial negative charge will be on carbon atom and positive one on lithium atom. It is a result of lithium much higher eagerness to give up its electron than that of a carbon. So the electron density of a polarized carbon-lithium bond will be closer to carbon atom.



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Polarization of a bond

Bond can be polarized even if it is formed between identical atoms (*e.g.* C-C). Bond can be influenced by groups or atoms having place further from a bond (in the same molecule or not) and influencing it from a distance. Electron cloud can be attracted or repelled from far away if certain atoms or their groups are present.

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Molecule polarity

If the resultant center of partial negative charge of a molecule (analog to center of mass in case of charge) is not at the same place as the resultant center of partial positive charge, then the molecule is **polar**. Polarity is a result of certain shape of electron cloud. It forms due to certain polarized bonds arrangement (*e.g.* asymmetric).



Non-polar molecules

Polar molecules

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Molecule dipole moment

- **Dipole moment (μ)** is a measure of molecules' polarity. The size of dipole moment is expressed as a product of charge [C] and distance between "centers" of negative and partial positive charges of a given molecule [m]. Unit of dipole moment is debye [$D = C \cdot m$].
- $1 D = 3.34 \cdot 10^{-30} C \cdot m$
- Polarity of solvents is often expressed as dielectric constant (relative permittivity).

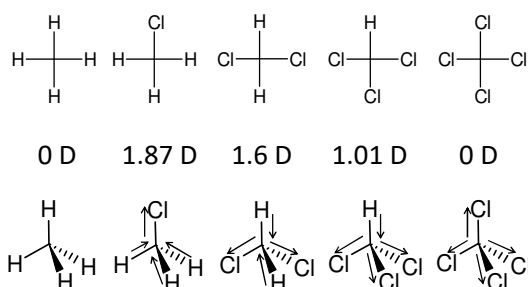
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Molecule polarity

- Polarity of a molecule determines various physical and chemical properties of substances, especially solvents. For instance, polar solvents (those which molecules are polar) dissolve ionic compounds, non-polar not. Polar compounds will (usually) dissolve better in polar solvents and non-polar compounds will dissolve better in non-polar.
- Also free electron pairs influence the polarity of a molecule.

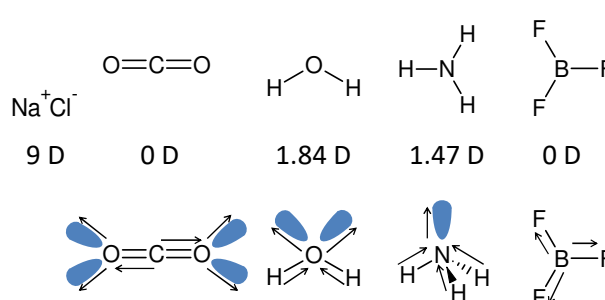
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Molecule polarity



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Molecule polarity



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Intermolecular interactions

- **Dipole-dipole:** between polar molecules (that have dipole moment); they repel and attract each other basing on electrostatics (+ attracts -, + repels +, - repels -). This kind of interaction determines physical properties of the compound (T_b , T_m , solubility);
- **Hydrogen bonds:** between molecules that have a partial positive charge on hydrogen atom (*i.e.* -OH or -NH groups) and nucleophilic centers (atoms that have free electron pairs);

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Intermolecular interactions

- **Van der Waals forces:** between non-polar molecules (that have no dipole moment); temporary non-uniform electron cloud distribution in a molecule (due to electrons movement) can form unstable weak dipole, that enables weak electrostatic interactions; those are short-range interactions, but if such molecules would get closer to each other (on shorter range than sum of van der Waals atomic radii of both atoms in contact) then they start to repel each other.

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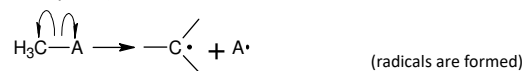
Covalent bond cleavage

- During reactions bonds usually cleave and subsequently new ones are formed. Organic compounds have mostly covalent bonds, thus this kind of bond usually cleaves. Covalent bond can cleave in two ways - homolytically (forming **radicals**) and heterolytically (forming **ions**).

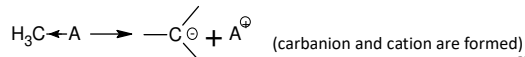
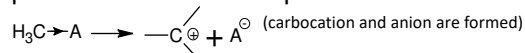
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Radicals and carboions

- Homolytic cleavage occurs in case of weakly polarized bonds and in weakly polar (or non-polar) solvents:



- Heterolytic cleavage occurs usually in case of polarized bonds and in polar solvents:



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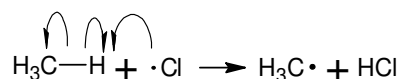
Radicals and carboions

- Carboions and radicals are usually unstable, so they are not final products of the reaction, but the **intermediate product** of the reaction.
- Cleavage of bonds occurs as a result of suitable conditions: temperature, solvent type (polar or non-polar) and under influence of right reagents/catalysts.

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Reactions with radical mechanism

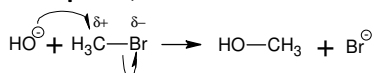
Non-polar compounds' (without dipole moment) reactions proceed involving radicals in a non-polar solvent and reagent that initiate reaction is also a radical (formed *in-situ*, which means during reaction, as an intermediate product).



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Reactions with ionic mechanism

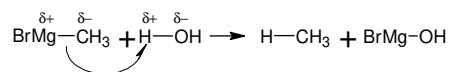
- Polar compounds' reactions proceed involving ions in a polar solvent and type of reagent that initiates reaction depends on a cleaved bond polarization direction.
- If carbon atom that forms bond that is about to cleave has partial positive charge, then it is an **electrophile** (it accept the electrons), and reagent that initiate the reaction is required to have free electron pair to share. Such reagent is called then the **nucleophile** (it looks for atoms that can accept its electrons).



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Reactions with ionic mechanism

- If carbon atom that forms bond that is about to cleave has partial negative charge, then it is a **nucleophile** (nucleophilic center), and reagent that initiate the reaction has to be an electrophile. It means that it looks for atoms/molecules/ions that lack electrons (nucleophiles) it can share with.



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Reactions with ionic mechanism

- Good nucleophiles are ions of atoms from the right side of periodic table (I^- , Br^- , Cl^- , OH^- , CN^-), molecules with free electron pair (H_2O , CH_3OH , NH_3) and groups with partial negative charge at the strongly polarized covalent bond (metalloorganic bonds, *e.g.* CH_3^-MgBr).
- Good electrophiles are ions with deficit of electrons: H^+ , H_3O^+ (it is not the same, only in water H^+ forms H_3O^+ instantly, in other solvents it occurs only if water molecules are present), NO_2^+ , carbocations (R^+) and groups with strong partial positive charge in strongly polarized compounds (H^+Br).

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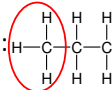
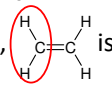
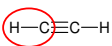
Reactions with double bond

- Double bonds do not cleave in a way that both parts of the bond would cease. Bond formed with π electrons is much weaker than that formed with σ electrons, so the former will always break first. Electrons from the π bond will be used in the first place during reaction (forming new bonds) with radicals and electrophiles. The same goes to triple bonds.

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Structural formulae

- Line between atoms represents the bond. Double line and triple line represent double and triple bond, respectively. In organic compounds' formulae all single C-C and C-H bonds are neglected, apart from those that are important to illustrate reaction mechanism for instance.
- In practice, simplified formulae are used, where atoms are grouped into CH_2 , CH_3 , CH , moieties, *etc.*

- *E.g.*:  is $CH_3CH_2CH_3$,  is $CH_2=CH_2$
and  is $CH\equiv CH$.

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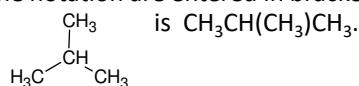
Structural formulae

- In case of general formulae, also numerous simplifications are used. For instance, halogen atoms are indicated as **X** and usually mean Cl, Br or I (fluorine less frequent as it is often separately indicated as F, due to its different properties).
- Metals are indicated as **M** (both alkaline and transition);
- Hydrocarbon groups are indicated as **R** (the closest bonds to the connection should be single ones and there should be no heteroatoms in the group); different moieties are indicated as **R¹**, **R²**, **R³**... , **R₁**, **R₂**, **R₃** or **R**, **R'**, **R''**, **R'''**...
- **Heteroatoms** are all atoms that are not carbon or hydrogen (usually means O, N, S, or less frequently, P).

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Structural formulae

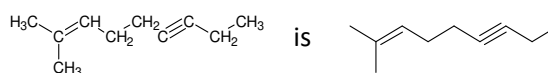
- In reaction schemes nucleophilic moiety is indicated as **Nu** and electrophilic one as **E**;
- Aromatic moiety is indicated as **Ar**;
- Common hydrocarbon groups are indicated as follows: CH_3^- as **Me**, $CH_3CH_2^-$ as **Et**, $CH_3CH_2CH_2^-$ as **Pr** (or **n-Pr**), $CH_3CH_2CH_2CH_2^-$ as **Bu** (or **n-Bu**).
- Branches from the main carbon chain in a single line notation are entered in brackets, *e.g.*:



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Structural formulae

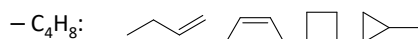
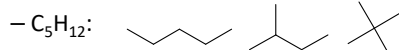
In larger, polyatomic formulae most of the notation is neglected. Only differences between fulfillment of all carbon bonds with hydrogens are indicated. Notation is thus simplified to carbon skeleton (including bonds multiplicity) and potential heteroatoms, *e.g.*:



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Isomerism

- Isomers are two (or more) different compounds, often of completely different properties, that have the same molecular formula, *e.g.*:

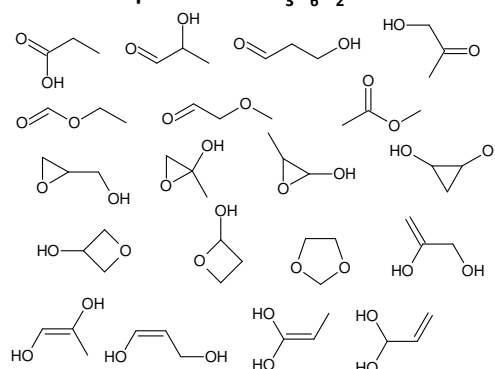


- As one can see, they may even belong to different classes of compounds.

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Isomerism

19 isomeric compounds with C₃H₆O₂ molecular formula:



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Carbon order

- Order of a given carbon atom is the number of other carbon atoms (with sp³ configuration) that are directly connected to it.
- Order of carbon results in a different reactivity of a given carbon – for instance, carbocation or *tert*-butyl radical (tertiary) are very stable, contrary to ethyl radical/carbocation (primary).

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Classification of organic compounds

- Saturated hydrocarbons** – contain C and H atoms only, connected with single bonds exclusively;
- Unsaturated hydrocarbons** – contain C and H atoms only, at least one C-C bond is double or triple;
- Cyclic hydrocarbons** – saturated or unsaturated hydrocarbons chain of which form a ring/loop at least once.
- Aromatic hydrocarbons** – contain C and H atoms only and at least one aromatic ring (usually 6-member);

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Classification of organic compounds

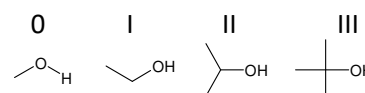
Compounds with **functional groups**, *i.e.* atoms group which provides main chemical (reactivity, stability) and physical (different state of matter even with identical molar mass and elemental composition) properties of a compound.

Halogenated compounds – derivatives of hydrocarbons, in which at least one hydrogen is substituted with halogen atom (F, Cl, Br, I);

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Classification of organic compounds



- Alcohols** contain **hydroxylic group** noted as -OH order of carbon to which the hydroxylic group is connected to indicates the alcohol order:



more -OH groups in a compound make it: **diol** (two OH groups) Or **triol** (three OH groups).
If -OH group is connected to aromatic ring, then it is a **phenol**.


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Classification of organic compounds

- **Aldehydes and ketones** – contain **carbonyl** group, noted as $-C(O)-$ ($R_1-C(O)-R_2$) or $>C=O$. Ketones contain carbonyl group at any carbon of the chain but terminal one. Aldehydes have this group at the end of carbon chain (at the terminal carbon). Carbonyl group on aldehyde is noted as $-CHO$:

- **Ethers and epoxides** – contain **ether** group, ($-O-$, R_1-O-R_2) although epoxides (usually considered as a subgroup of ethers) contain it exclusively as a 3-member ring:




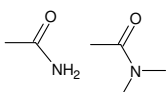

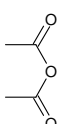
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Classification of organic compounds

- **Carboxylic acids** contain **carboxyl** group (combination of carbonyl and hydroxylic groups) with a possibility of deprotonation (like inorganic acids). Acidic group formula is $-COOH$, or sometimes $-CO_2H$. Acid radical formula is $-COO^-$. Organic acids can be multi-carboxylic. Carboxylic acids have numerous derivative compounds.


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Classification of organic compounds

- Carboxylic acids derivatives:
 - **Carbonyl chlorides** ($-COCl$):

 - **Esters** ($-COO-$, $R_1-COO-R_2$):

 - **Amides** ($-CONH_2$ or $R_1-CON(R_2)R_3$):

 - **Nitriles (cyanides)** ($-CN$): $\equiv N$

 - **Anhydrides** ($-C(O)OC(O)-$, $R-C(O)OC(O)-R$) or mixed anhydrides ($R_1-C(O)OC(O)-R_2$):



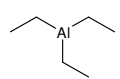
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Classification of organic compounds

- **Amines** – contain **amine** group $-NH_2$. Amines can be of various order, *i.e.*:
 Primary amines contain $-NH_2$ group
 Secondary contain $-NH-$ group (R_1-NH-R_2)
 Tertiary contain $-N<$ group ($R_1-N(R_2)-R_3$)
- **Nitro compounds** – contain **nitro** group $-NO_2$

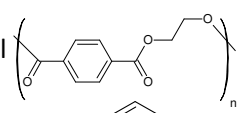
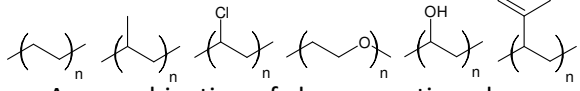
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Classification of organic compounds

- **Thiols** – contain **thiol** group $-SH$
- **Sulfonic compounds** – contain **sulfonic** group $-SO_3H$

- **Metalloorganic** – contain metals, *e.g.*:
 $R-Li$, $R-MgX$, $R_1-Al(R_2)-R_3$, *etc.*


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Classification of organic compounds

- **Polymers** – compounds that are built of repeated identical groups of atoms (structural units mers) – $R_1-(R_2)_n-R_3$, *e.g.*:


- Any combination of above-mentioned;
- Many, many others...

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