

STUDY GUIDE FOR CHAPTER 2

- Classification of Hydrocarbons:
 - Aliphatic:
 - Alkanes – contain only C – C single bonds;
 - Alkenes – contain C = C double bonds;
 - Alkynes – contain C = C triple bonds;
 - Aromatic – the most common among them are the compounds which contain benzene rings.
- Theories of bonding - there are two theories to describe the covalent bonding:
 - Valence Bond Theory – two atoms, as they approach each other, have their appropriate orbitals overlap, each orbital containing a single electron. The result of the overlap is the formation of an electron pair, which is shared by both atoms and this amounts to the formation of a bond between the two atoms. The strength of the bond depends on the amount and type of orbital overlap. The bond created when two H-atoms overlap their s-orbitals is of a type where the overlap occurs along the axis connecting the nuclei. This kind of bond is known as a σ -bond. How close can two atoms approach each other when bonding? There is a distance at which their attraction is strongest (bond distance!!!). If they get closer, then there is a strong repulsion, due to the positive – positive interaction of the nuclei. If they are too far apart, then attraction is small.
 - Molecular Orbital Theory – the idea behind is that much like atoms, electrons in molecules can also be described by wave functions, which in this case are called molecular orbitals (MOs). Molecular orbitals are obtained by the linear combination of atomic orbitals (LCAO). In other words, unlike the valence bond theory, MO theory says that atomic orbitals lose their identity, once the bonding occurs, to form totally new entities – MOs. The rule here is: The number of combined atomic orbitals MUST equal the number of generated MOs. If we combine two atomic orbitals, then two MOs are generated – a bonding and an antibonding. In the case of the hydrogen molecule the orbitals are called σ -bonding (a parallel with the σ -bond!!) and σ^* -antibonding. Antibonding orbitals are always marked with an asterisk. The bonding orbitals are lower in energy than the starting atomic orbitals while the antibonding are higher (by the same amount). In certain cases there are MOs formed, whose energy is the same as that of the starting atomic orbitals. They are called non-bonding.
- Hybridization and molecular geometry. What are the predictions based on electronic structure? What are the actual facts on the geometry and shape of organic molecules? The need to introduce hybridization – LCAO of the same atom. Types of hybridization:
 - sp^3 – four sp^3 orbitals, tetrahedral geometry. Formation of methane and ethane. Other molecules – NH_3 , NH_4^+ , H_2O . Both bonds and lone pairs count for hybridization;
 - sp^2 – three sp^2 orbitals, trigonal geometry. One p -orbital unhybridized, perpendicular to the hybrid orbitals. The structure of ethylene – how is the double bond formed? Other molecules – formaldehyde (HCHO) and BH_3 ;
 - sp – two sp -orbitals, linear geometry. Two p -orbitals unhybridized, perpendicular to the hybrid orbitals and to each other. The structure of acetylene – how is the triple bond formed? Other molecules – HCN , BeH_2 .Now consider some more complex examples: acetonitrile (CH_3CN) or acetaldehyde (CH_3CHO).
How to determine hybridization: Count s -bonds + lone pairs = # of hybrid orbitals
What happens when there is resonance – hybridization at particular center is identified as the lowest possible.
- Isomers in the alkane series – the first three alkanes have no constitutional isomers. Starting with butane, such isomers are possible and do exist. There is no simple (or analytical) way to predict the number of isomers for a particular number of carbons in the molecule.

5. Nomenclature of Alkanes - with the exception of the first four members (methane, ethane, propane, butane) all the rest are named based on the root of the Greek word for the particular number of carbon atoms, with the suffix *-ane*. Also, if necessary, additional prefixes are attached to denote a particular isomer. Thus, pentane, isopentane, neopentane. The systematic approach to naming compounds and the set of rules, which governs it, is usually called ***nomenclature***. Several have been suggested and practiced in the past, but the contemporary and accepted is the IUPAC nomenclature. Names, given in accordance with IUPAC are known as IUPAC names or *systematic* names, unlike the pre-IUPAC names, which are known as *common* or *trivial*.

A. Nomenclature of acyclic alkanes – there is an established set of rules as to how to name alkanes:

- 1) Form the base for the compounds' name. This is the name of the longest continuous carbon chain (*main chain*) in the molecule. Other groups attached to the main chain are considered as *substituents*. If two chains of equal length can be found in a particular molecule, use the one that gives a greater number of substituents.
- 2) Number the main chain, starting with the end, which is nearest a substituent.
- 3) The substituents names are derived in the same fashion as the parent hydrocarbons, but instead of suffix *-ane*, put a suffix *-yl*. Thus, methane – methyl, pentane – pentyl, heptane – heptyl, etc. The substituents also take prefixes, whenever necessary, to differentiate between different isomeric substituents. Several possibilities: a) if the substituent is a straight chain, then nothing or *n-* (for normal); b) *iso-*, if it contains the *iso*-group at the end of the chain; With the exception of the isopropyl, all other *iso*-groups, as well as all *n*-groups have a carbon atom attached to the main chain, which is connected to only one other carbon atom. Such carbon atoms are known as *primary* (1°). Examples. If this carbon is connected to two other carbon atoms, then the substituent receives the prefix *sec-*. Such carbon atoms are known as *secondary* (2°). Examples. If this carbon atom is bound to three more carbons, then prefix *tert-*. Such carbon atoms are known as *tertiary* (3°).
- 4) When two or more substituents are present, list the substituents in alphabetical order. If some of them are identical, list them together with a prefix identifying their total number: *di-* (two), *tri-* (three), *tetra-* (four), *penta-* (five), etc. Do not alphabetize these prefixes!
- 5) When a more complex substituent is encountered, one may need, for the naming of the substituent, to apply the entire procedure outlined above, i.e. select a main chain, etc. But as usual, the substituent as whole should always bear the suffix *-yl*, instead of *-ane*. The chain selected to serve as the base for the name of the substituent **MUST** contain the carbon atom directly bound to the main chain of the molecule. This carbon atom is always number 1, when the atoms of the substituent's chain have to be numbered.

B. Nomenclature of cycloalkanes – the prefix *cyclo-* is added to the name for the unbranched alkanes with the same # of carbon atoms. Thus propane (three C) – cyclopropane; pentane (five C) – cyclopentane. Numbering is done in such a fashion that the sum of all numbers (locants) is the smallest possible.

6. Physical Properties of Alkanes and Cycloalkanes.

A. Boiling Points – increase regularly for unbranched alkanes and increase regularly for branched alkanes (Two separate plots!!). Boiling points and other physical properties influenced by the intermolecular forces.

a. Intermolecular forces. Three types:

- 1) *Dipole – dipole force* (what kind of molecules, how does it affect boiling point?)
- 2) *Dipole – Induced Dipole force*.

- 3) *London dispersion force* (what kind of molecules, what is the nature of this force, how does it appear, how does it depend on molecular size and shape? Examples). London forces are the major type of attractive forces between non-polar molecules, such as alkane molecules.
- B. Melting Points – also dictated by the London dispersion forces.
- C. Solubility – what is the general rule for solubility – “*like dissolves like*”. Four cases: 1) *Polar solute in polar solvent* – dissolves, reason; 2) *Polar solute in a nonpolar solvent* – does not dissolve, reason; 3) *Nonpolar solute in a polar solvent* – does not dissolve, reason; 4) *Nonpolar solute in a nonpolar solvent* – dissolves, reason, the role of entropy.
7. Chemical Properties of Alkanes.
- A. Combustion – all alkanes (in fact all hydrocarbons) burn in oxygen atmosphere, to form carbon dioxide and water. This is the process behind automobile engine, thermal power plants, etc. The reaction occurs with the release of substantial amount of heat – heat of combustion. As in other cases, it is the enthalpy difference between products and reactants. Products are always the same – CO₂ and water. Therefore, the combustion reaction can be used to evaluate the differences in the heat content between various constitutional isomers. Turns out that more highly branched alkanes have lower heat contents, i.e. lower potential energy. **STABILITY OF ISOMERS IN CHEMISTRY IS EVALUATED IN THIS FASHION: THE LOWER THE POTENTIAL ENERGY OF A PARTICULAR ISOMER, THE MORE STABLE IT IS.** Remember this!
- B. Redox reactions in organic chemistry – they are concerned with the oxidation state (or number) of one or more carbon atoms in a particular molecule, which may change in the course of a reaction. An elegant way to assign oxidation numbers is given in Table 2.5 in the textbook. **AS A RULE: WHEN THE OXIDATION NUMBER AT A PARTICULAR CENTER INCREASES, THIS CENTER IS BEING OXIDIZED. IF IT DECREASES, THE CORRESPONDING CENTER IS REDUCED.**

After this lecture you should have high confidence and knowledge on the following topics:

- Have knowledge about σ -bonds and π -bonds – nature, strength;
- Have firm knowledge about hybridization – types and how this affects molecular geometry. Be able to determine the hybridization of a particular center.
- Have firm knowledge on nomenclature – rules, naming compounds, producing a structure on the basis of an IUPAC name;
- Learn the names and structures of the most common substituents: methyl, ethyl, propyl, isopropyl, butyl, isobutyl, *sec*-butyl, *t*-butyl;
- Be able to determine a type of carbon – primary, secondary, tertiary, quaternary;