Carey Chapter 2 – Hydrocarbon Frameworks: “Alkanes”

Hydrocarbons

- Aliphatic
- Aromatic

Alkanes    Alkenes    Alkynes

2.2-2.3 Chemical Bonding

1s orbitals of two hydrogen atoms

In-phase overlap of two 1s orbitals gives new orbital encompassing both hydrogen atoms

Figure 2.3 – Valence bond picture for H₂
2.2-2.3 Chemical Bonding – Two Possibilities

Figure 2.5 – bond and antibond possibilities for H₂

2.4 Molecular orbitals by combining two atomic orbitals

Figure 2.6 – bond and antibond possibilities for H₂
2.5 Introduction to Alkanes – Methane, Ethane, Propane

CH₄
b.p. -160 °C

CH₃CH₃
-89 °C

CH₃CH₂CH₃
-42 °C

Figure 2.7 – Low molecular weight alkanes

2.6 sp³ Hybridization and bonding in Methane

Figure 2.9 – Hybridization picture for C in CH₄
2.6 sp³ Hybridization and bonding in Methane

![Image of methane molecule with hybrid orbital picture for C in CH₄]

Figure 2.10 – Hybrid orbital picture for C in CH₄

2.7 sp³ Hybridization and bonding in Ethane

![Image of ethane molecule with sp³-sp³ interaction in ethane]

Figure 2.11 – sp³-sp³ interaction in ethane
2.8 Isomeric alkanes – the Butanes

- Structural Isomers
  - $\text{C}_4\text{H}_{10}$, $n$-butane
  - $\text{C}_4\text{H}_{10}$, isobutane

2.9-2.10 Higher alkanes – the $\text{C}_5\text{H}_{12}$ isomers

- Structural Isomers
  - $\text{C}_5\text{H}_{12}$, $n$-pentane
  - $\text{C}_5\text{H}_{12}$, isopentane
  - $\text{C}_5\text{H}_{12}$, neopentane
2.10 Higher alkanes – diversity

### TABLE 2.1
The Number of Constitutionally Isomeric Alkanes of Particular Molecular Formulas

<table>
<thead>
<tr>
<th>Molecular formula</th>
<th>Number of constitutional isomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>1</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>1</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>1</td>
</tr>
<tr>
<td>C₄H₁₀</td>
<td>2</td>
</tr>
<tr>
<td>C₅H₁₂</td>
<td>3</td>
</tr>
<tr>
<td>C₆H₁₄</td>
<td>5</td>
</tr>
<tr>
<td>C₇H₁₆</td>
<td>9</td>
</tr>
<tr>
<td>C₈H₁₈</td>
<td>18</td>
</tr>
<tr>
<td>C₉H₂₀</td>
<td>35</td>
</tr>
<tr>
<td>C₁₀H₂₂</td>
<td>75</td>
</tr>
<tr>
<td>C₁₁H₂₄</td>
<td>4,347</td>
</tr>
<tr>
<td>C₁₂H₂₆</td>
<td>366,319</td>
</tr>
<tr>
<td>C₁₃H₂₈</td>
<td>62,491,178,805,831</td>
</tr>
</tbody>
</table>

Careful with drawing chains!

All the same compound!
2.11-2.12 Alkane nomenclature - Need to know up to C-12

IUPAC Rules:

- Find the longest continuous carbon chain
- Identify substituent groups attached to the chain
- Number the chain so as to keep numbers small
- Write the name in the following format:

Numerical location - [substituent(s)][parent alkane]

* e.g. 2,3-dimethylheptane
2.12 IUPAC Rules and how to apply them

Hexane (IUPAC); n-hexane (common)

2-methylhexane not 5-methylhexane

2,4-dimethylheptane

2.13 Alkyl groups - Classes

Replace -ane ending with -yl

primary (1°)  secondary (2°)  tertiary (3°)
### 2.13 Alkyl groups - Common

- **Propyl group**: $\text{CH}_3\text{CH}_2\text{CH}_2\text{H}$
- **Isopropyl group** (1-methylethyl): $(\text{CH}_3)_2\text{CH}_2\text{H}$
- **t-Butyl group** (1,1-dimethylethyl): $(\text{CH}_3)_3\text{C}_2\text{H}$

### 2.14 Highly branched alkanes

- **4-Ethyl octane**
- **4-Ethyl-3-methyloctane**
- **4-Ethyl-3,5-dimethyloctane**
2.15 Cycloalkanes

1,1,3-trimethylcyclohexane

2-ethyl-1,1-dimethylcyclopentane

(notice the “di” is not involved in the alphabetization)

2.16 Sources of alkanes and cycloalkanes

Figure 2.12 – Various fractions obtained from crude oil
2.17 Physical properties

Figure 2.15 – Boiling point versus number of carbons

2.17 Physical properties – branched alkanes

Figure 2.16 – How branching has an effect on properties
2.18 Chemical properties of Alkanes

Alkane properties:
- Generally very insoluble in water ("greasy" or "oily")
- Individual molecules interact via van der Waals forces
- These intermolecular forces decrease with branching
- Alkanes may be combusted in oxygen:

\[
\text{e.g. } \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad \Delta H = -213 \text{ kcal}
\]

i.e. combustion of hydrocarbons releases energy

2.18 Heats of combustion – Figure 2.17
**2.19 Oxidation-Reduction in Organic Chemistry**

**TABLE 2.4 Oxidation Number of Carbon in One-Carbon Compounds**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structural formula</th>
<th>Molecular formula</th>
<th>Oxidation number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>CH₄</td>
<td>−4</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH₃OH</td>
<td>CH₃O</td>
<td>−2</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>H₂C=O</td>
<td>CH₂O</td>
<td>0</td>
</tr>
<tr>
<td>Formic acid</td>
<td>HOCO</td>
<td>CH₂O₂</td>
<td>+2</td>
</tr>
<tr>
<td>Carbonic acid</td>
<td>HOCO₂</td>
<td>H₂CO₃</td>
<td>+4</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>O=C=O</td>
<td>CO₂</td>
<td>+4</td>
</tr>
</tbody>
</table>

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**2.20 sp² Hybridization in ethylene**

Figure 2.18 – Different representations of ethene
2.20 sp² Hybridization in ethylene

Figure 2.19 – Hybrid orbitals required for ethylene

2.20 sp² Hybridization in ethylene

Figure 2.20
2.21 sp Hybridization in acetylene

Figure 2.22

Figure 2.23