2.13
Sources of Alkanes and Cycloalkanes

Crude oil

Naphtha
(bp 95-150 °C)

C_5-C_{12}

Kerosene
(bp: 150-230 °C)

C_{12}-C_{15}

Light gasoline
(bp: 25-95 °C)

Crude oil

C_{15}-C_{25}

Gas oil
(bp: 230-340 °C)

Refinery gas

C_1-C_4

Residue

Petroleum refining

Cracking

converts high molecular weight hydrocarbons
to more useful, low molecular weight ones

Reforming

increases branching of hydrocarbon chains
branched hydrocarbons have better burning characteristics for automobile engines

2.14
Physical Properties of Alkanes and Cycloalkanes

Boiling Points of Alkanes

governed by strength of intermolecular attractive forces

alkanes are nonpolar, so dipole-dipole and dipole-induced dipole forces are absent

only forces of intermolecular attraction are induced dipole-induced dipole forces

Induced dipole-Induced dipole attractive forces

two nonpolar molecules

center of positive charge and center of negative charge coincide in each

Induced dipole-Induced dipole attractive forces

movement of electrons creates an instantaneous dipole in one molecule (left)

Induced dipole-Induced dipole attractive forces

temporary dipole in one molecule (left) induces a complementary dipole in other molecule (right)

Induced dipole-Induced dipole attractive forces

temporary dipole in one molecule (left) induces a complementary dipole in other molecule (right)

Induced dipole-Induced dipole attractive forces

the result is a small attractive force between the two molecules

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Boiling Points

increase with increasing number of carbons

more atoms, more electrons, more opportunities for induced dipole-induced dipole forces

decrease with chain branching

branched molecules are more compact with smaller surface area—fewer points of contact

Boiling Points

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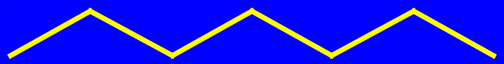
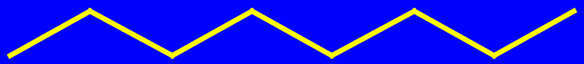


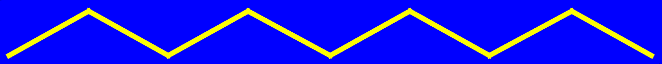
Heptane

bp 98°C



Octane

bp 125°C



Nonane

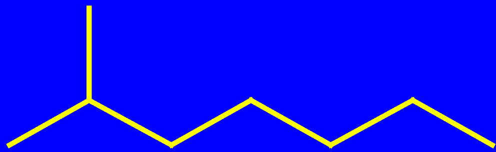
bp 150°C

Boiling Points

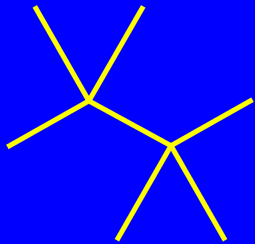
decrease with chain branching

branched molecules are more compact with smaller surface area—fewer points of contact with other molecules

Octane: bp 125°C



2-Methylheptane: bp 118°C



2,2,3,3-Tetramethylbutane: bp 107°C

2.15
Chemical Properties.
Combustion of Alkanes

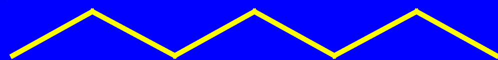
All alkanes burn in air to give carbon dioxide and water.

Heats of Combustion

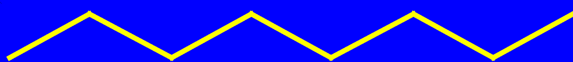
increase with increasing number of carbons

more moles of O_2 consumed, more moles of CO_2 and H_2O formed

Heats of Combustion

Heptane  4817 kJ/mol

654 kJ/mol

Octane  5471 kJ/mol

654 kJ/mol

Nonane  6125 kJ/mol

Heats of Combustion

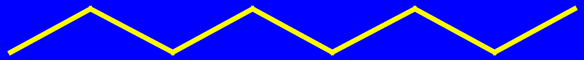
increase with increasing number of carbons

more moles of O_2 consumed, more moles of CO_2 and H_2O formed

decrease with chain branching

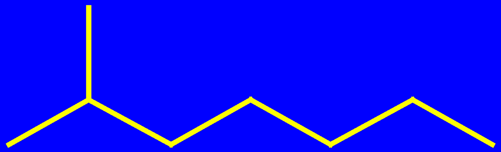
branched molecules are more stable (have less potential energy) than their unbranched isomers

Heats of Combustion



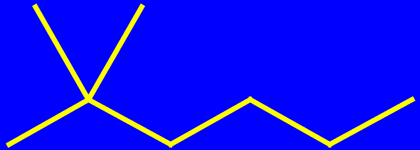
5471 kJ/mol

5 kJ/mol



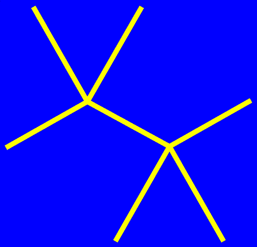
5466 kJ/mol

8 kJ/mol



5458 kJ/mol

6 kJ/mol



5452 kJ/mol

Important Point

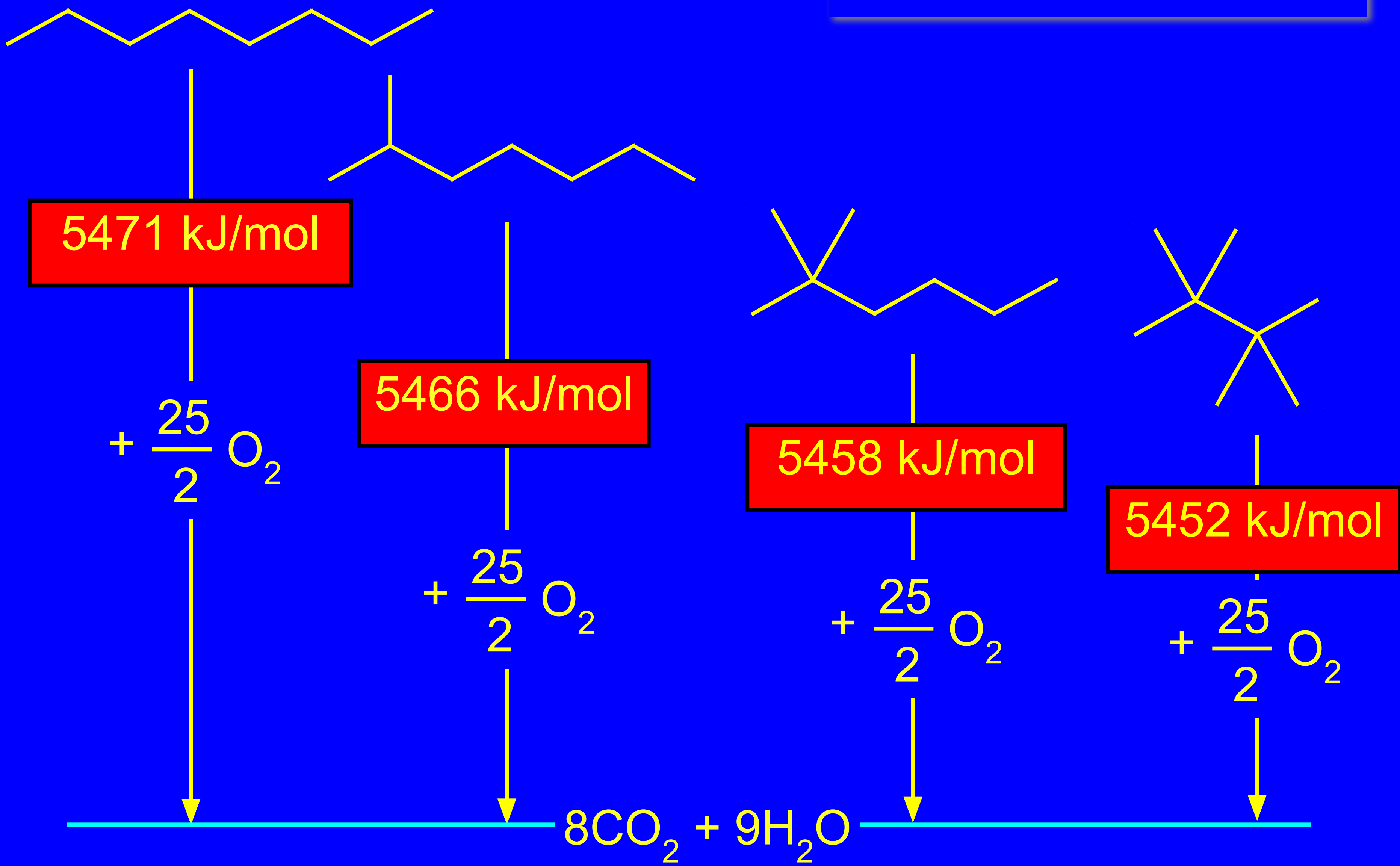
Isomers can differ in respect to their stability.

Equivalent statement:

Isomers differ in respect to their potential energy.

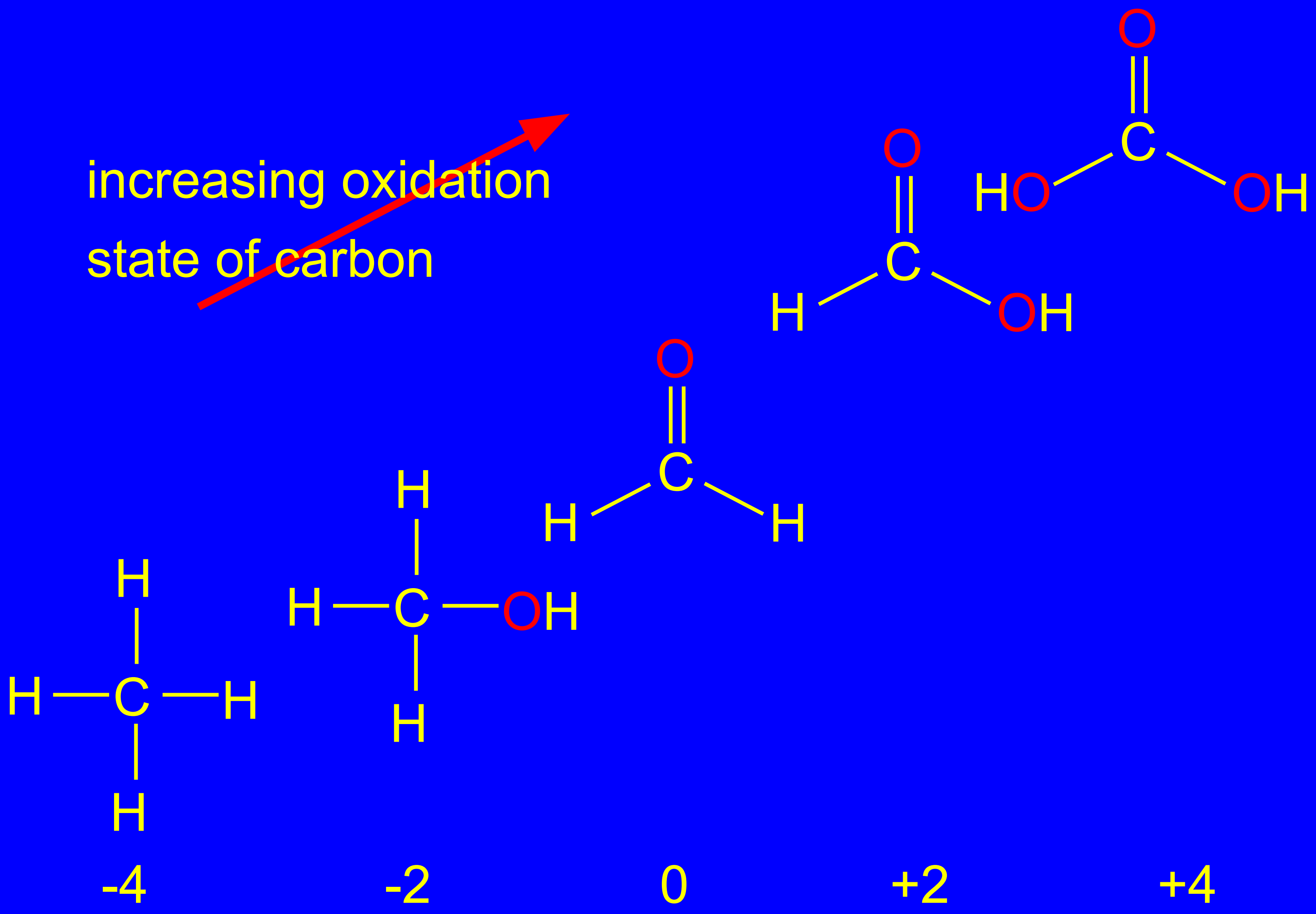
Differences in potential energy can be measured by comparing heats of combustion.

Figure 2.5


5471 kJ/mol
5466 kJ/mol
5458 kJ/mol
5452 kJ/mol
$+ \frac{25}{2} O_2$
$+ \frac{25}{2} O_2$
$+ \frac{25}{2} O_2$
$+ \frac{25}{2} O_2$
$8CO_2 + 9H_2O$

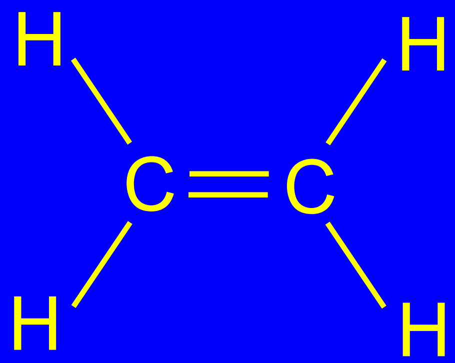
2.16
Oxidation-Reduction in Organic Chemistry

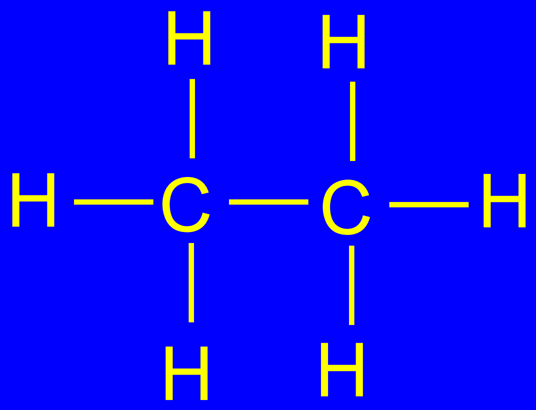
Oxidation of carbon corresponds to an increase in the number of bonds between carbon and oxygen and/or a decrease in the number of carbon-hydrogen bonds.


increasing oxidation
state of carbon
H
H
C
H
H
H
H
C
OH
H
O
C
H
H
O
C
H
OH
O
C
HO
OH
-4
-2
0
+2
+4

increasing oxidation state of carbon

$HC\equiv CH$





-3 -2 -1

But most compounds contain several (or many) carbons, and these can be in different oxidation states.

Working from the molecular formula gives the average oxidation state.

CH_3CH_2OH

-3 (arrow to CH_3)

-1 (arrow to CH_2)

C_2H_6O

Average oxidation state of C = -2

Fortunately, we rarely need to calculate the oxidation state of individual carbons in a molecule .

We often have to decide whether a process is an oxidation or a reduction.

Generalization

Oxidation of carbon occurs when a bond between carbon and an atom which is less electronegative than carbon is replaced by a bond to an atom that is more electronegative than carbon. The reverse process is reduction.

$$-\overset{|}{\underset{|}{C}}-X \;\xrightleftharpoons[\text{reduction}]{\text{oxidation}}\; -\overset{|}{\underset{|}{C}}-Y$$

X less electronegative than carbon

Y more electronegative than carbon

Examples

Oxidation

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

Reduction

$$CH_3Cl + 2Li \longrightarrow CH_3Li + LiCl$$