

Organic Chemistry 1

Lecture 4

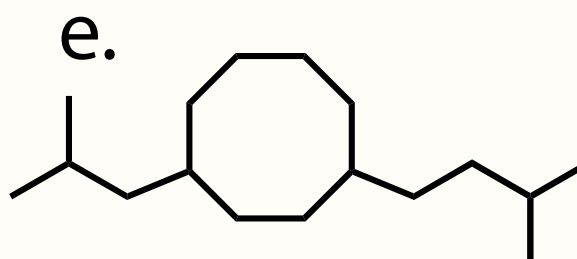
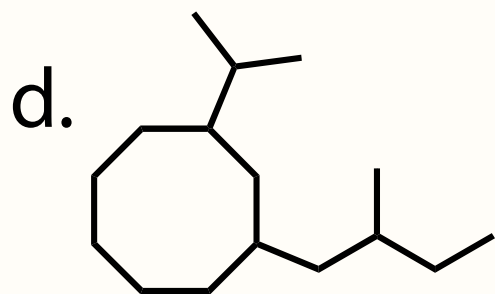
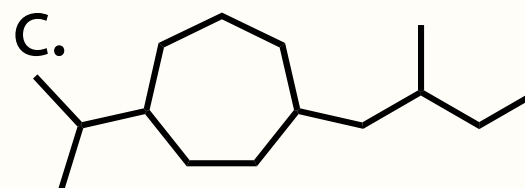
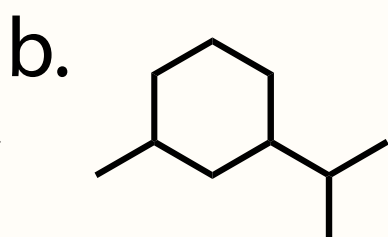
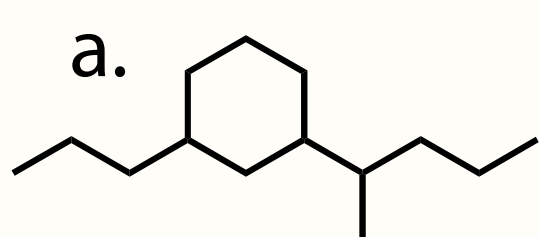
Instructor: Prof. Duncan Wardrop

Time/Day: T & R, 12:30-1:45 p.m.

January 21, 2010

Self Test Question

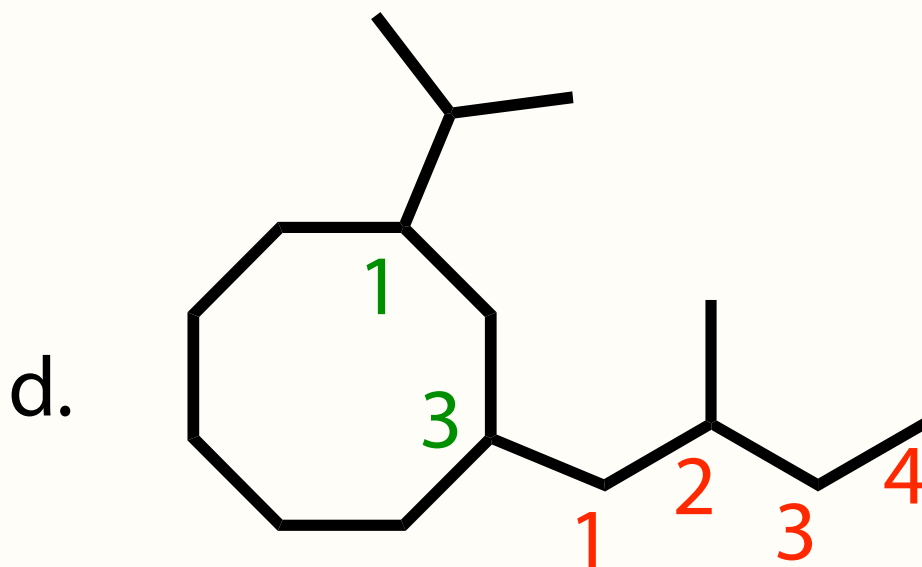
Which structure below represents
1-isopropyl-3-(2-methylbutyl)cyclooctane?



- A. a
- B. b
- C. c
- D. d
- E. e

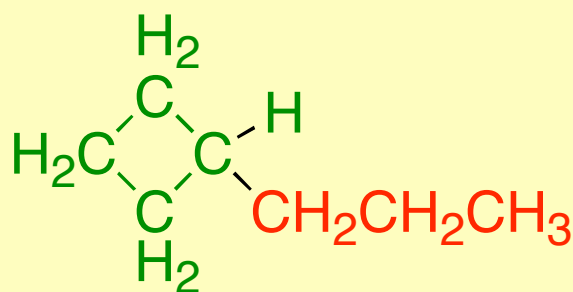
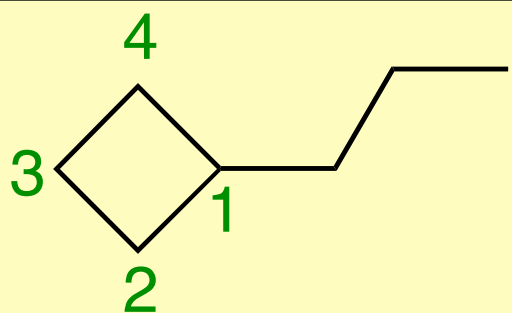
Self Test Question

Which structure below is
1-isopropyl-3-(2-ethylbutyl)cyclooctane?



- A. a
- B. b
- C. c
- D. d
- E. e

IUPAC: Monosubstituted Cycloalkanes



propylcyclobutane

Steps:

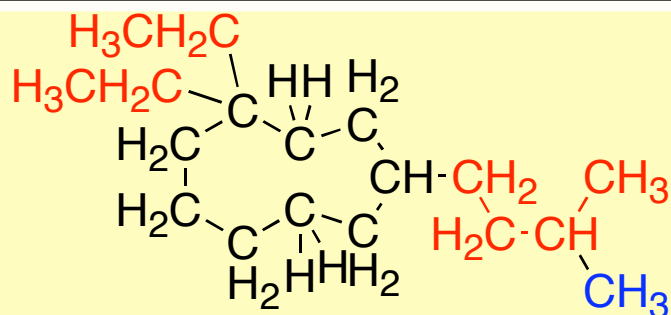
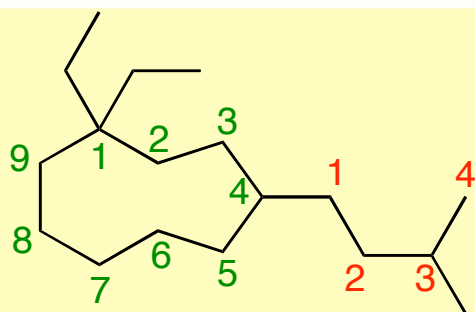
1. Count the number of carbons in the ring. Precede the parent name with *cyclo*.
2. Identify straight chain, common or branched substituent groups.
3. Name the compound according to the figure below.

Conventions:

- If the number of carbons in the substituent is greater, name the ring as a cycloalkyl substituent (e.g. cyclobutyl)
- If the ring is monosubstituted, no locant is necessary; substituent locant is assumed to be 1.



IUPAC: Polysubstituted Cycloalkanes



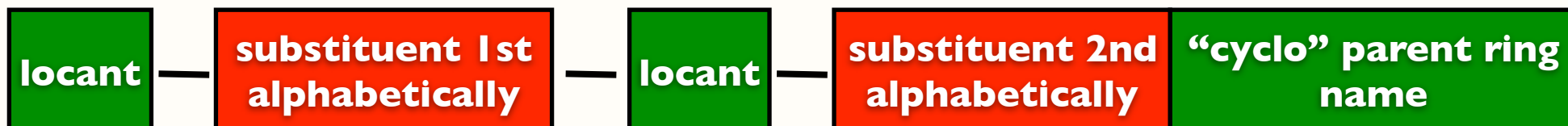
1,1-diethyl-4-(3-methylbutyl)cyclononane

Steps:

1. Count the number of carbons in the ring. Precede the parent name with *cyclo*.
2. Identify straight chain, common or branched substituent groups.
3. Name the compound according to the figure below.

Conventions:

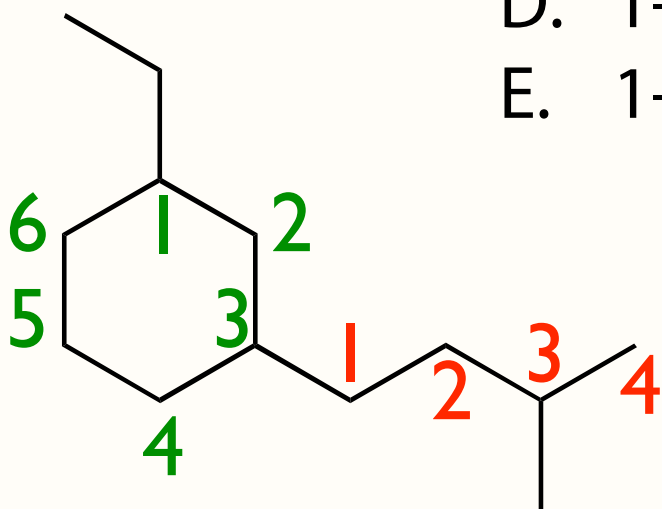
- If the number of carbons in the substituent is greater, name the ring as a cycloalkyl substituent (e.g. cyclobutyl). Follow all previous steps and conventions for naming substituents.
- List substituents in alphabetical order. Ignore replicating prefixes.
- First, follow first point of difference rule. If two numbering schemes give the same locants, name the molecule so that the first alphabetical substituent has the lower locant value.



Self Test Question

What is the IUPAC name for the molecule below?

- A. 1-ethyl-3-pentylcyclohexane
- B. 3-ethyl-1-pentylcyclohexane
- C. 1-ethyl-3-(3-methylbutyl)cyclohexane
- D. 1-butyl-3-ethylcycloheptane
- E. 1-(2-methylbutyl)-3-ethylcyclohexane



* If two numbering schemes give the same locants, name the molecule so that the first alphabetical substituent has the lower locant value

Physical Properties of Alkanes

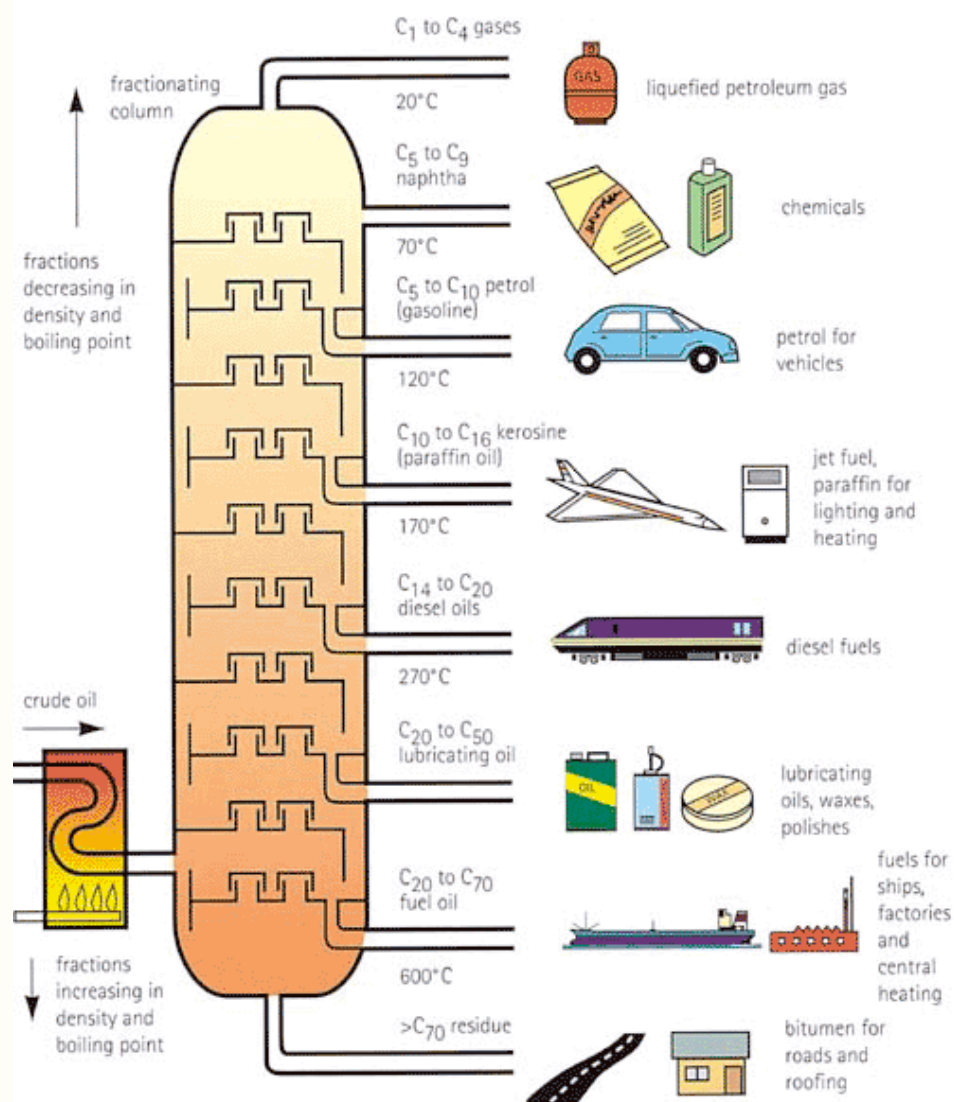
Sections: 2.16-2.17

Crude Oil - Source of Alkanes

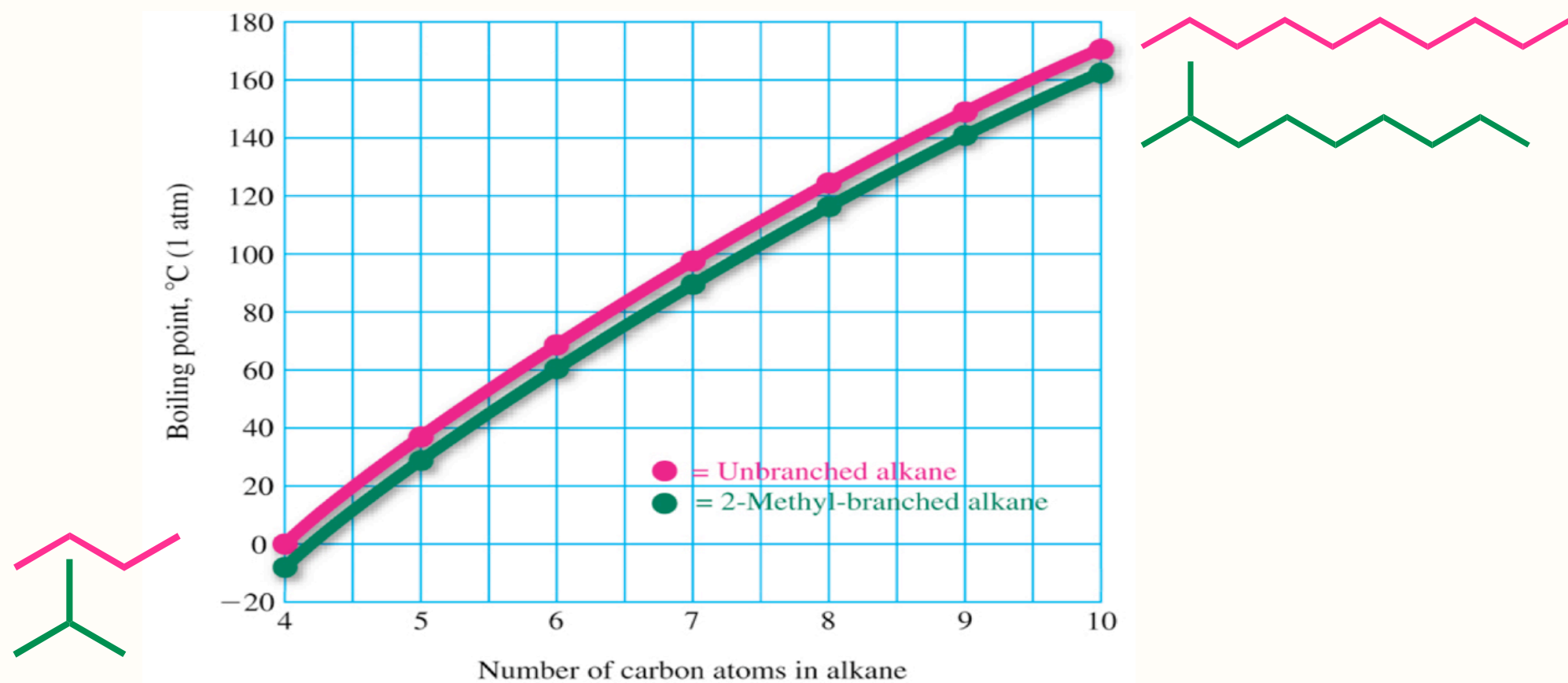
distillation: (physical separation) increases branching of the hydrocarbon chains; branched hydrocarbons have better burning characteristics

cracking: (chemical change) converts high molecular weight hydrocarbons to more useful, lower molecular weight fragments

reforming: (chemical change) increases branching of the hydrocarbon chains; branched hydrocarbons have better burning characteristics



Boiling Points Increase with # of Carbons



- boiling point increases with increasing number of carbon atoms
- branched alkanes have lower boiling points than unbranched isomers

Intermolecular Attractive Forces

van der Waals forces (VWF):

intermolecular attraction between neutral species

- ✗ 1. dipole-dipole (including hydrogen bonding)
- ✗ 2. dipole/induced-dipole
- ✓ 3. induced-dipole/induced-dipole (London dispersion)

- alkanes are non-polar; dipole-dipole & dipole/induced-dipole forces absent
- only forces of attraction between non-polar compounds are induced-dipole/induced-dipole

Induced-Dipole/Induced-Dipole (London Dispersion Forces)

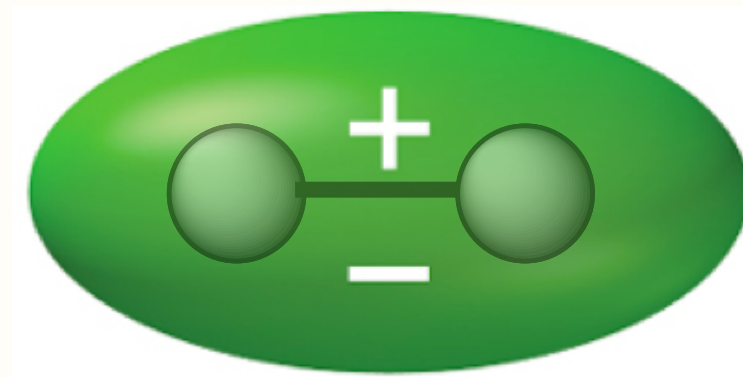
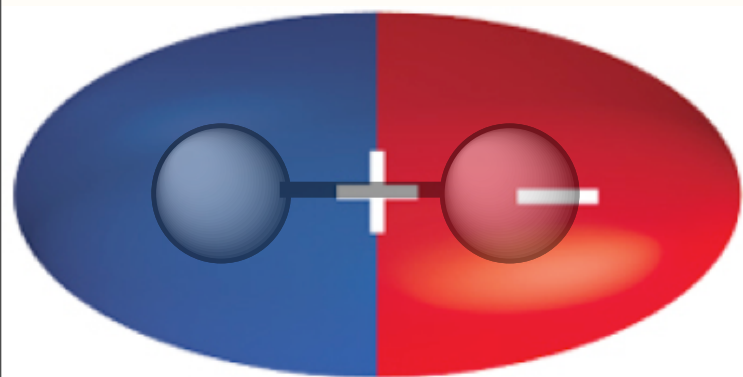
initial picture: centers of positive and negative charge in each individual molecule are identical



- green = electric field of surrounding two covalently bonded nuclei
- a.k.a. cumulative electron cloud

Induced-Dipole/Induced-Dipole (London Dispersion Forces)

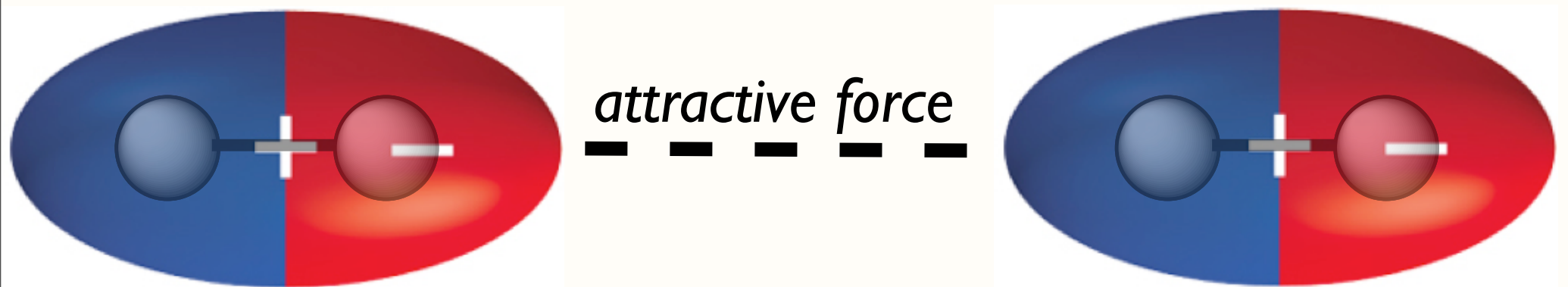
induced dipole in left molecule: movement of electrons creates instantaneous dipole in left molecule



- constant motion of electrons in orbitals
- blue/red: separation of positive and negative areas of charge within the electric field of molecule
- caused by asymmetric distribution of electrons

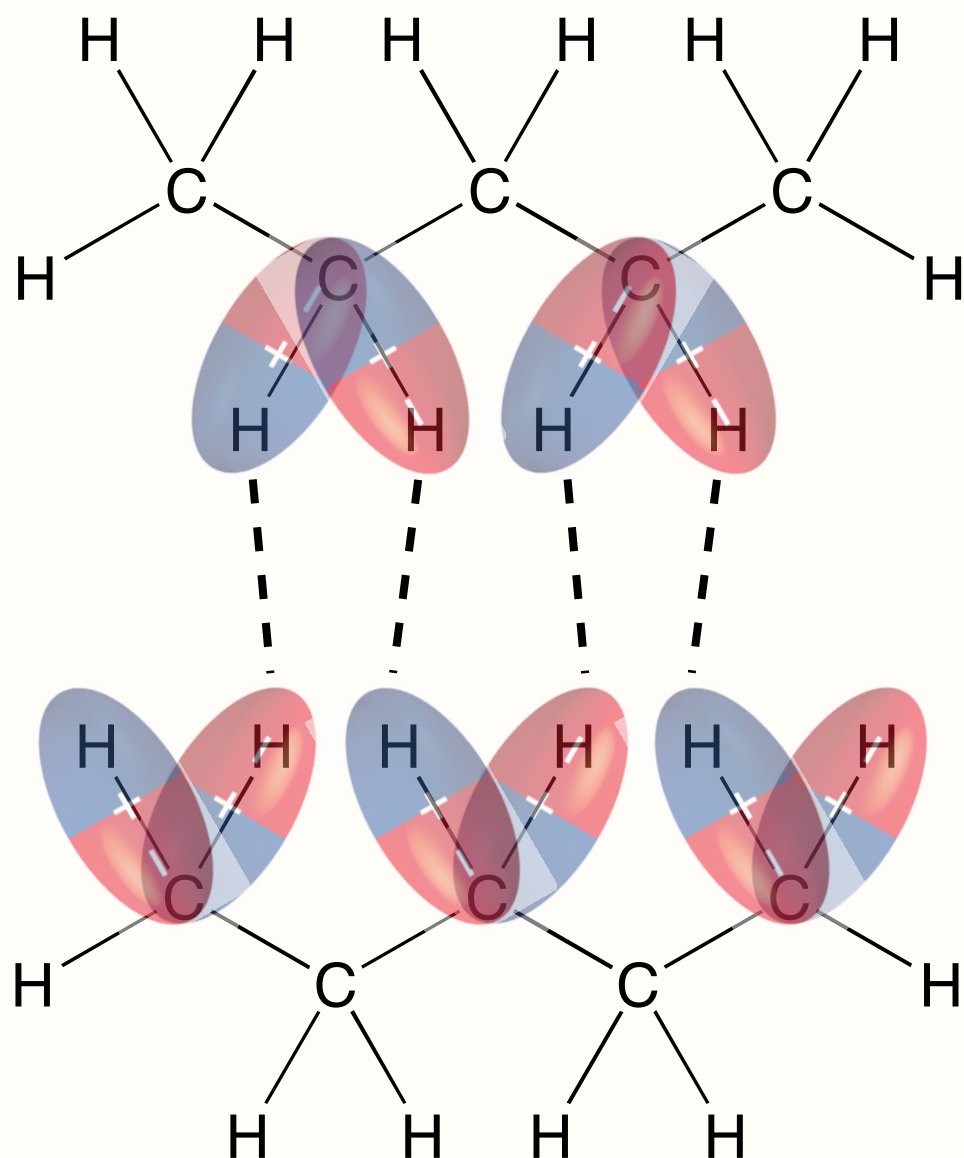
Induced-Dipole/Induced-Dipole (London Dispersion Forces)

left dipole induces right dipole: electron cloud in right molecule spontaneously adjusts to complement left



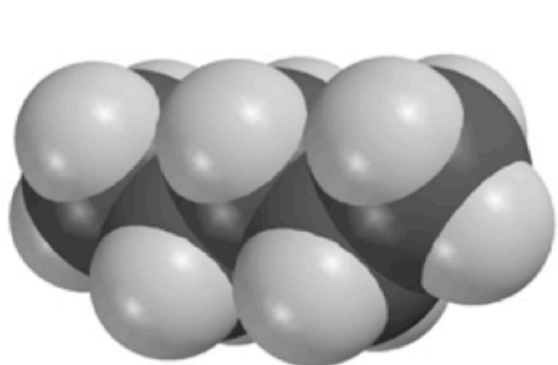
- electric attraction between two molecules
- both electric fields fluctuate, but always in the direction that produces weak attraction
- more atoms = more electrons = more induced dipoles = more attractive forces = higher boiling points

Induced-Dipole/Induced-Dipole (London Dispersion Forces)

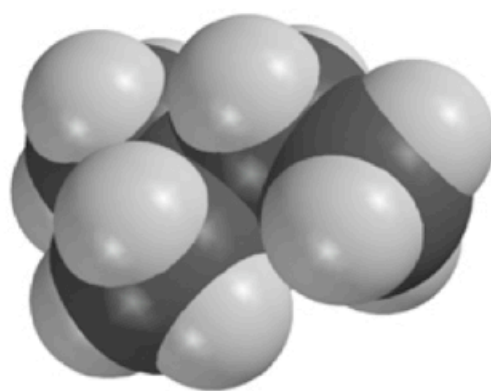


more atoms =
more electrons =
more induced dipoles =
more attractive forces =
higher boiling point

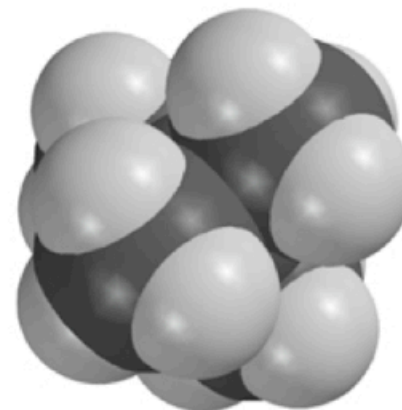
London VWFs in Branched Alkanes



(a) Pentane: $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
unbranched



(b) 2-Methylbutane:
 $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$



(c) 2,2-Dimethylpropane:
 $(\text{CH}_3)_4\text{C}$ highly branched

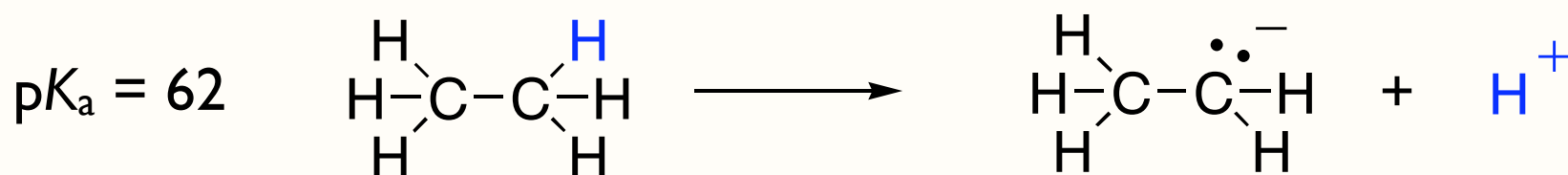
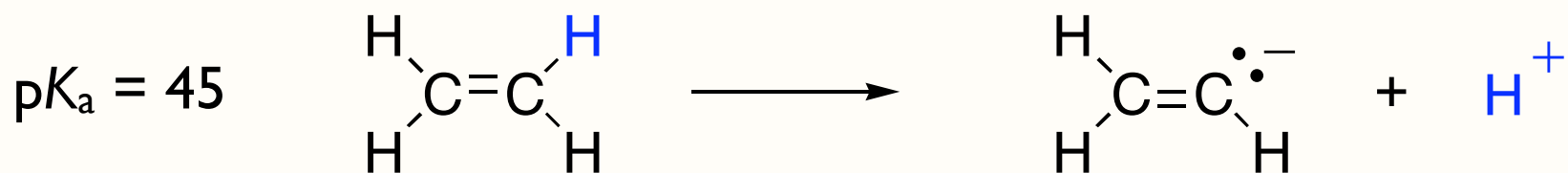
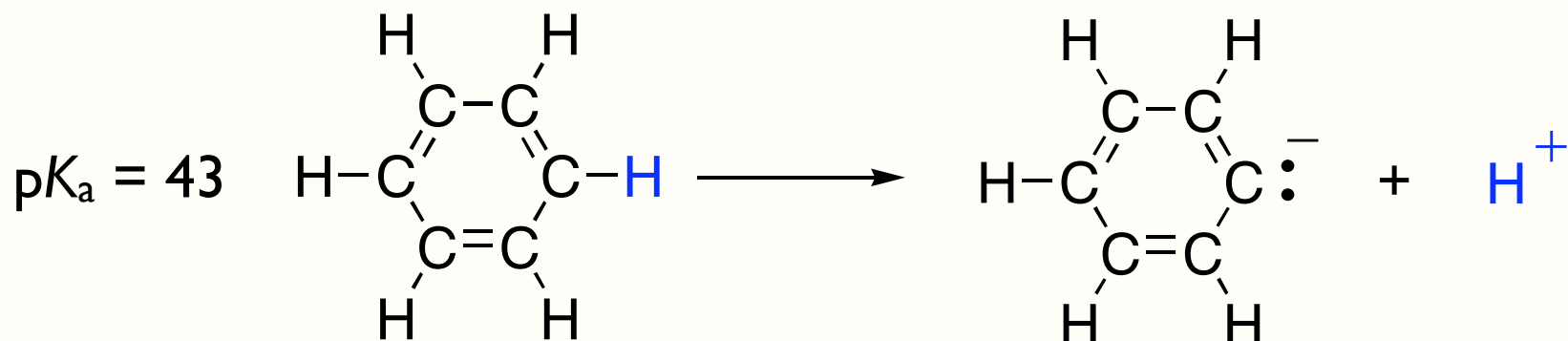
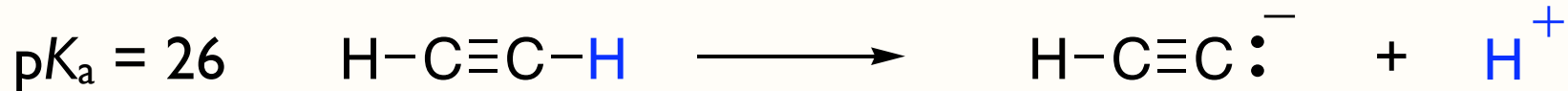
← Increasing Surface Area

← Increasing London Dispersion Forces

Chemical Properties of Alkanes

Sections: 2.16-2.17

Hydrocarbons are Weak Acids (Carbanions are Strong Bases)



Combustion is Exothermic

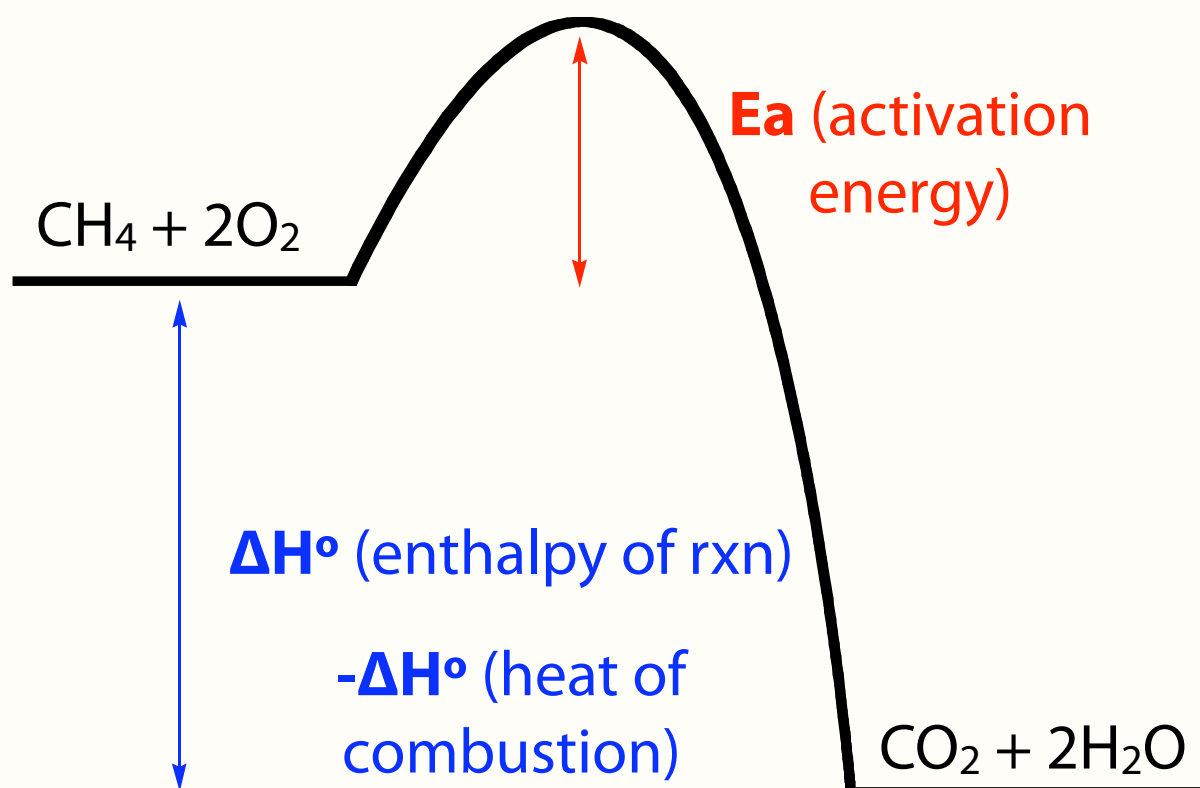
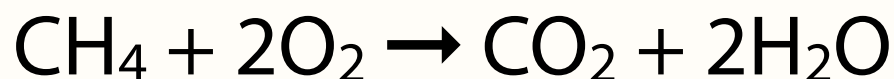
higher potential energy of reactant hydrocarbon =
larger enthalpy of combustion

$$\Delta H^\circ = H^\circ_{(\text{products})} - H^\circ_{(\text{reactants})}$$

exothermic
 $\Delta H^\circ = \text{negative}$

endothermic
 $\Delta H^\circ = \text{positive}$

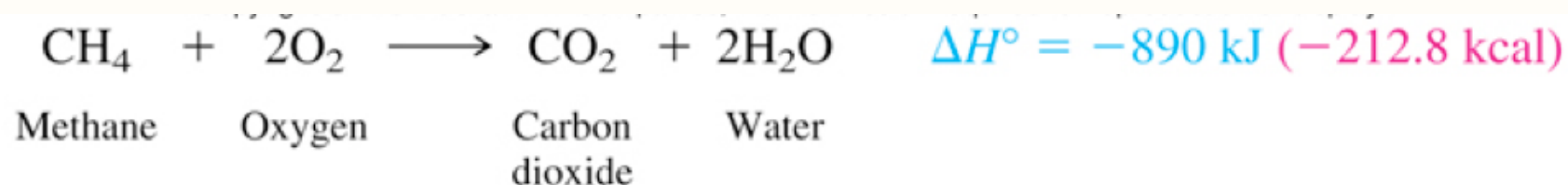
higher energy of reactants =
larger heat of combustion =
more exothermic



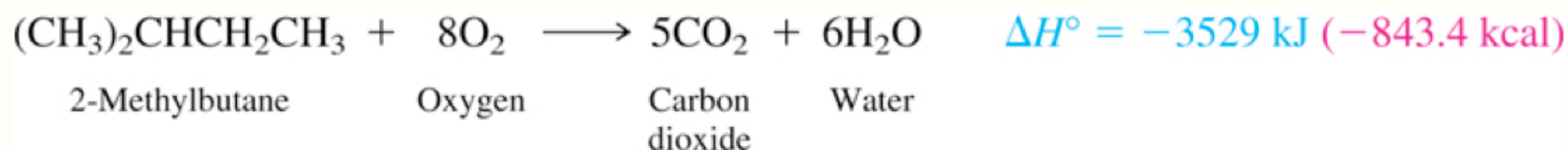
Enthalpy of Reaction & Heat of Combustion

$$\text{heat of combustion} = -\Delta H^\circ$$

$$\text{heat of combustion} = -\Delta H^\circ = 890 \text{ kJ (212.8 kcal)}$$



$$\text{heat of combustion} = -\Delta H^\circ = 3529 \text{ kJ (843.4 kcal)}$$



Heats of Combustion of Unbranched Alkanes

increase number of carbon atoms =
increased heat of combustion ($-\Delta H^\circ$)

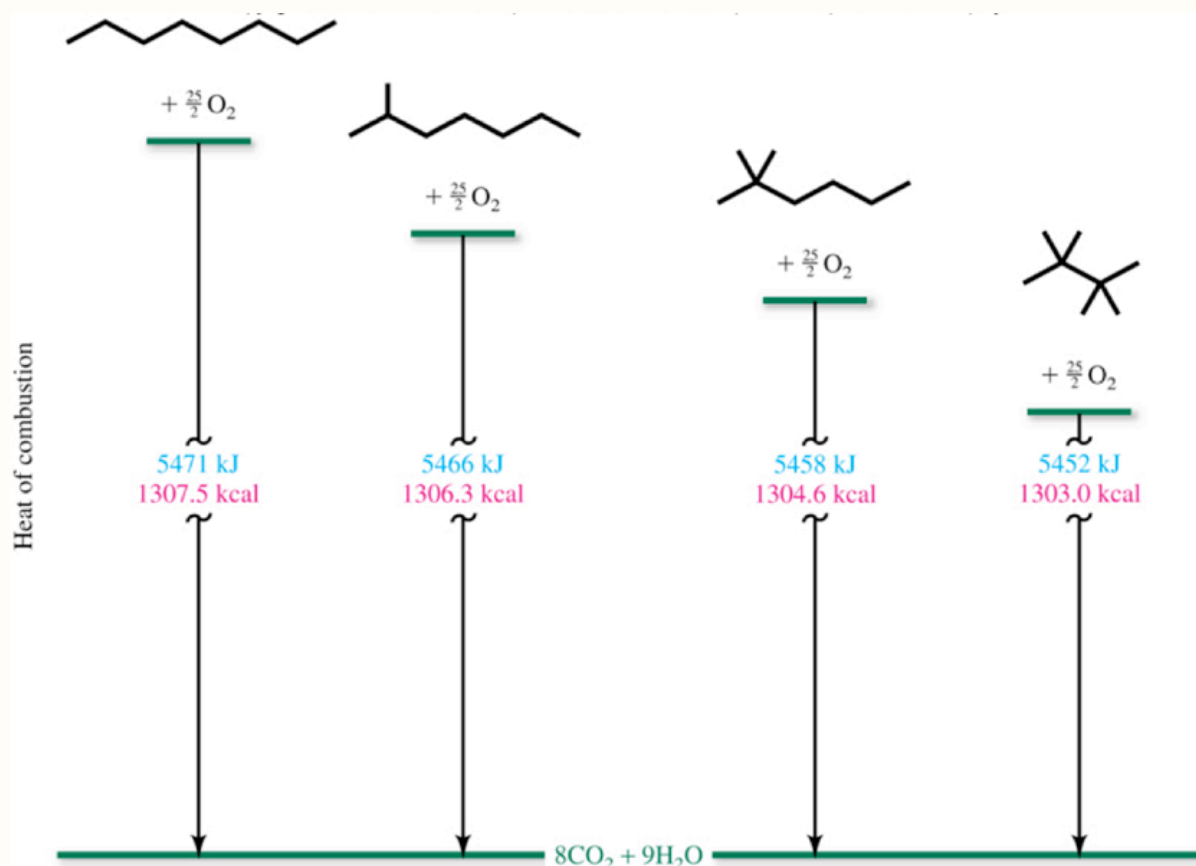
TABLE 2.3

Heats of Combustion ($-\Delta H^\circ$) of Representative Alkanes

Compound	Formula	$-\Delta H^\circ$	
		kJ/mol	kcal/mol
Unbranched alkanes			
Hexane	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	4,163	995.0
Heptane	$\text{CH}_3(\text{CH}_2)_5\text{CH}_3$	4,817	1,151.3
Octane	$\text{CH}_3(\text{CH}_2)_6\text{CH}_3$	5,471	1,307.5
Nonane	$\text{CH}_3(\text{CH}_2)_7\text{CH}_3$	6,125	1,463.9
Decane	$\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	6,778	1,620.1
Undecane	$\text{CH}_3(\text{CH}_2)_9\text{CH}_3$	7,431	1,776.1
Dodecane	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$	8,086	1,932.7
Hexadecane	$\text{CH}_3(\text{CH}_2)_{14}\text{CH}_3$	10,701	2,557.6

Heats of Combustion of Unbranched Alkanes

increased branching of *isomers* = increased
intramolecular VWF = lower energy (more stable) =
decreased heat of combustion ($-\Delta H^\circ$)



intramolecular forces:

same electronic forces
previously described

more nuclear attractions &
more intramolecular VWF =

more stable =

lower energy =

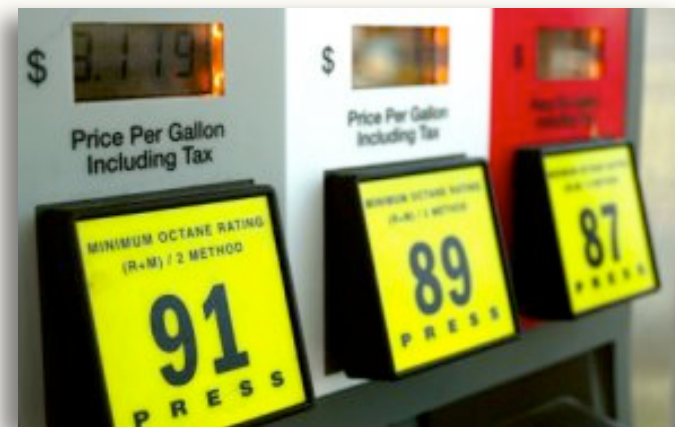
smaller heat of combustion

Octane Rating

0: heptane

higher heat of combustion
faster burning

lower heat of combustion
slower burning

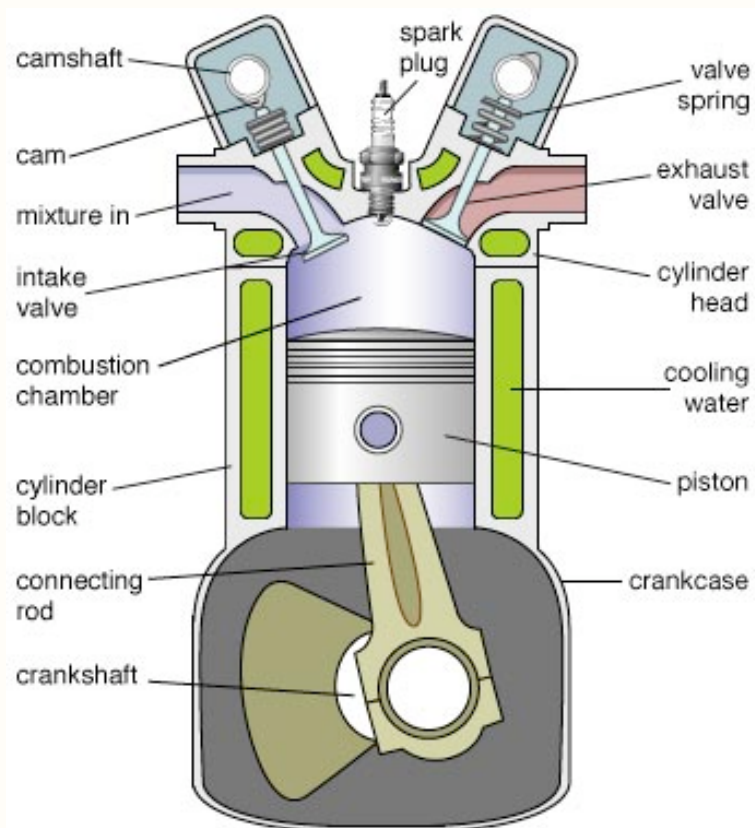


The burning qualities (knocking) of gasoline are compared to the burning qualities of *iso*-octane and heptane mixtures. This does NOT mean that gasoline contains *iso*-octane and heptane.

100: *iso*-octane (2,2,4-trimethylpentane)

Internal-Combustion Engine: Knocking

More highly branched alkanes produce less energy, but burn more effectively in an internal combustion engine by reducing knocking.



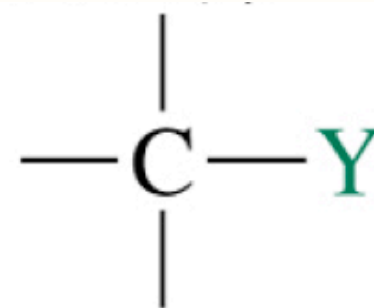
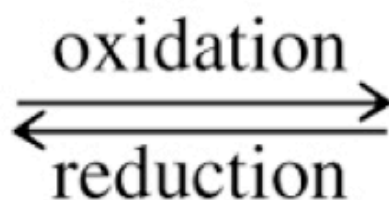
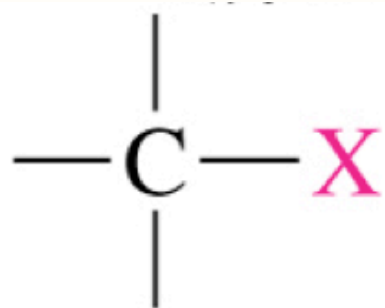
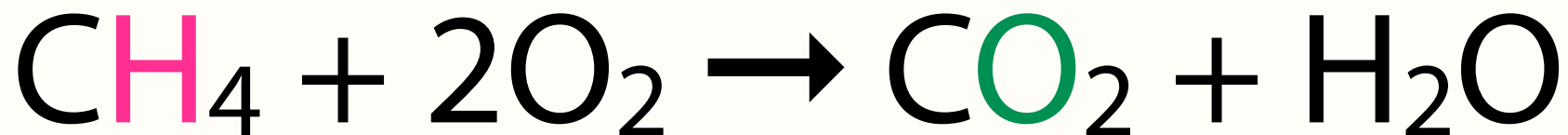
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engine-knocking or detonation: spontaneous combustion of the remaining fuel/air mixture left in the combustion chamber *after* normal combustion burn initiated by spark-plug

pre-ignition: spontaneous combustion of the fuel/air mixture *before* the spark plug fires

<http://www.streetrodstuff.com/Articles/Engine/Detonation/>

Combustion is an Oxidation Reaction



X is less electronegative
than carbon

Y is more electronegative
than carbon

Definitions of Oxidation and Reduction

Oxidation

(sometimes represented as [O])

- a. lose electrons (LEO GER)
- b. gain bonds to oxygen
- c. lose bonds to H
- d. oxidation # increases

Reduction

(sometimes represented as [H] or [R])

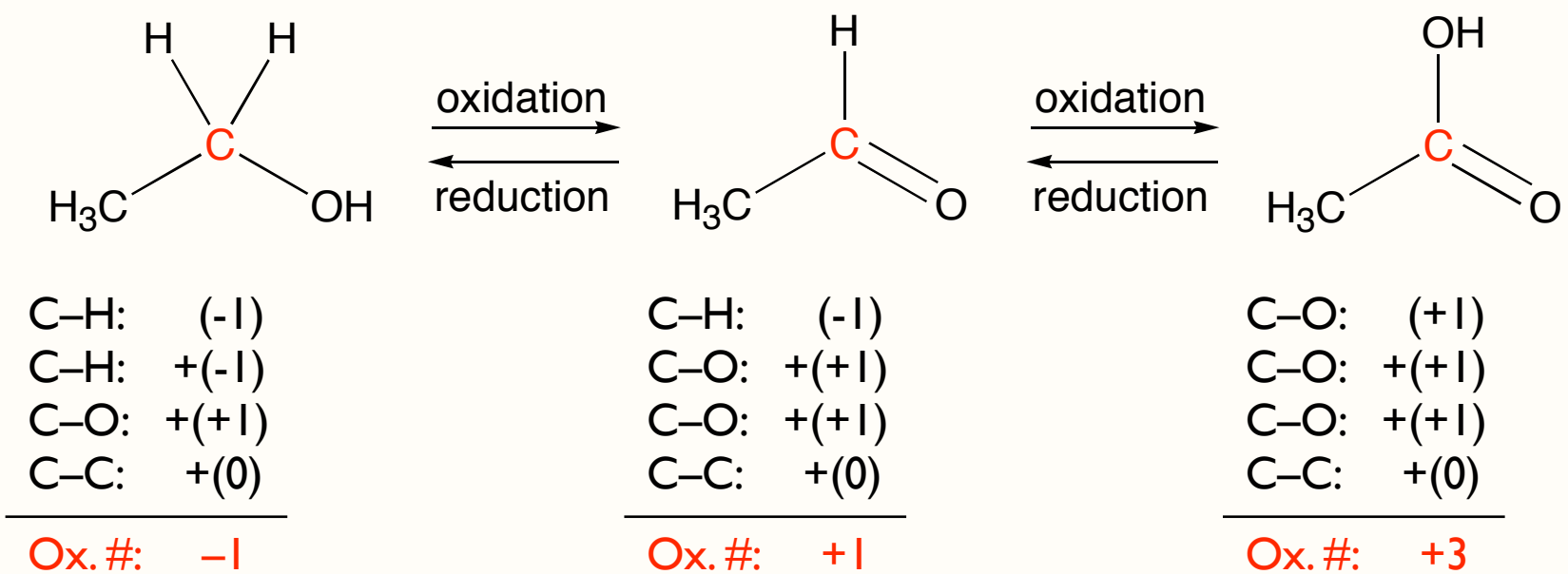
- a. gain electrons (LEO GER)
- b. lose bonds to oxygen
- c. gain bonds to H
- d. oxidation # decreases

All definitions above describe the amount of electron density centered on an atom. In summary, any process that decreases electron density, whether formal or informal, is termed oxidation. Likewise, any process that increases electron density, whether formal or informal, is termed reduction.

Determining Oxidation Numbers on Carbon

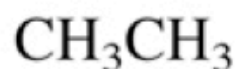
Three Simple Rules:

1. For each bond to an atom less electronegative than carbon (i.e. H) add (-1).
2. For each bond to an atom more electronegative than carbon (i.e. O) add (+1).
3. For each bond to another carbon atom add (+0).



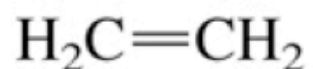
Oxidation States of Carbon

Increasing oxidation state of carbon
(decreasing hydrogen content)



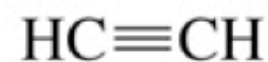
Ethane
(6 C—H bonds)

-3



Ethylene
(4 C—H bonds)

-2



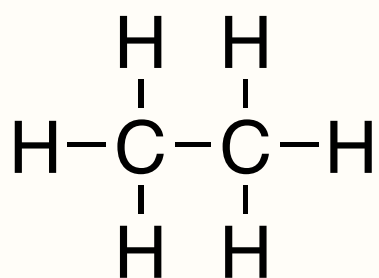
Acetylene
(2 C—H bonds)

-1

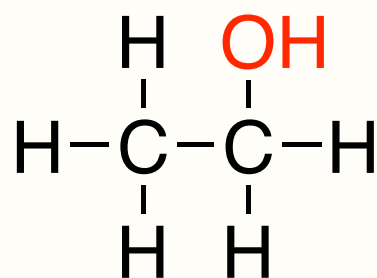
smaller number (more negative) = more electron density

Oxidation States of Carbon

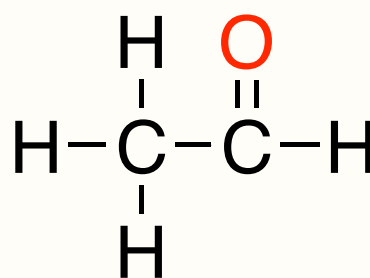
increasing oxidation state of carbon
(increasing number of bonds to oxygen)



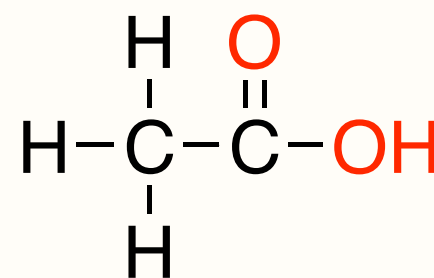
-3, -3



-3, -1



-3, +1

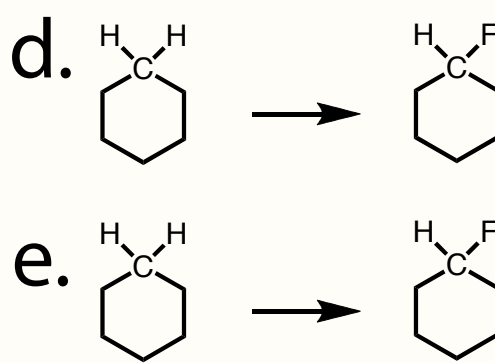
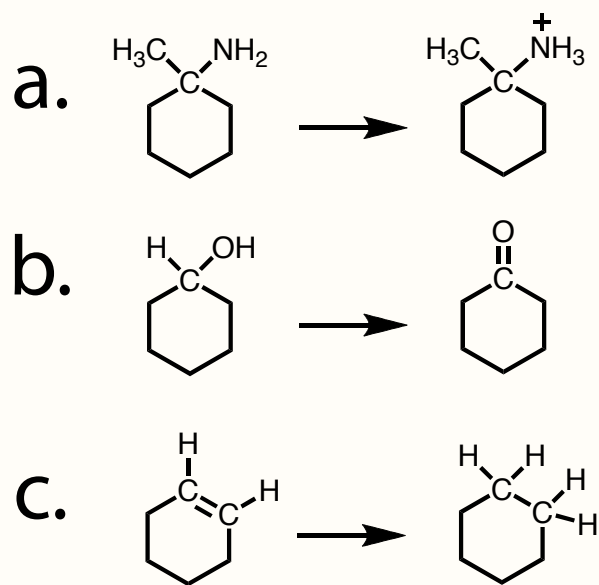


-3, +3

each carbon atom can have a different oxidation number

Self Test Question

Which process does *not* represent oxidation on carbon?

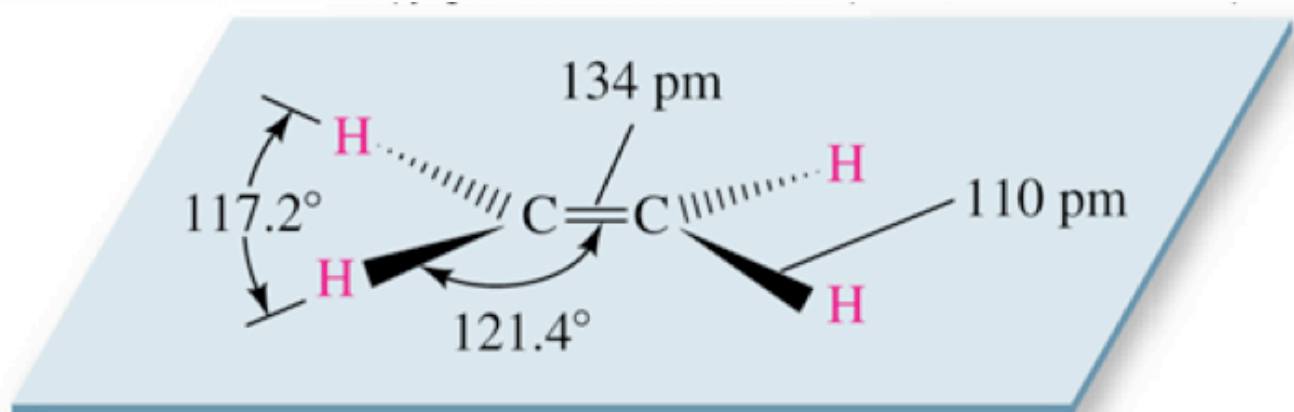


- A. a
- B. b
- C. c
- D. d
- E. e

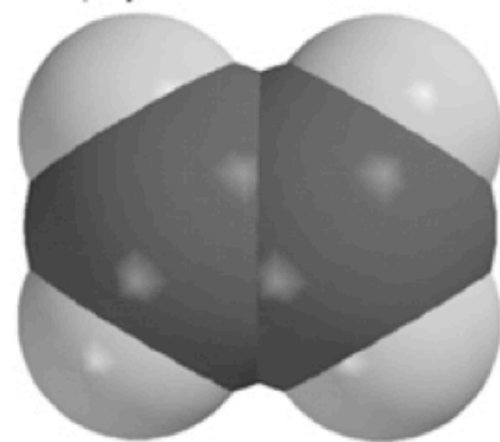
Alkenes and Alkynes: sp^2 & sp Hybridization

Sections: 2.20-2.22

Alkenes



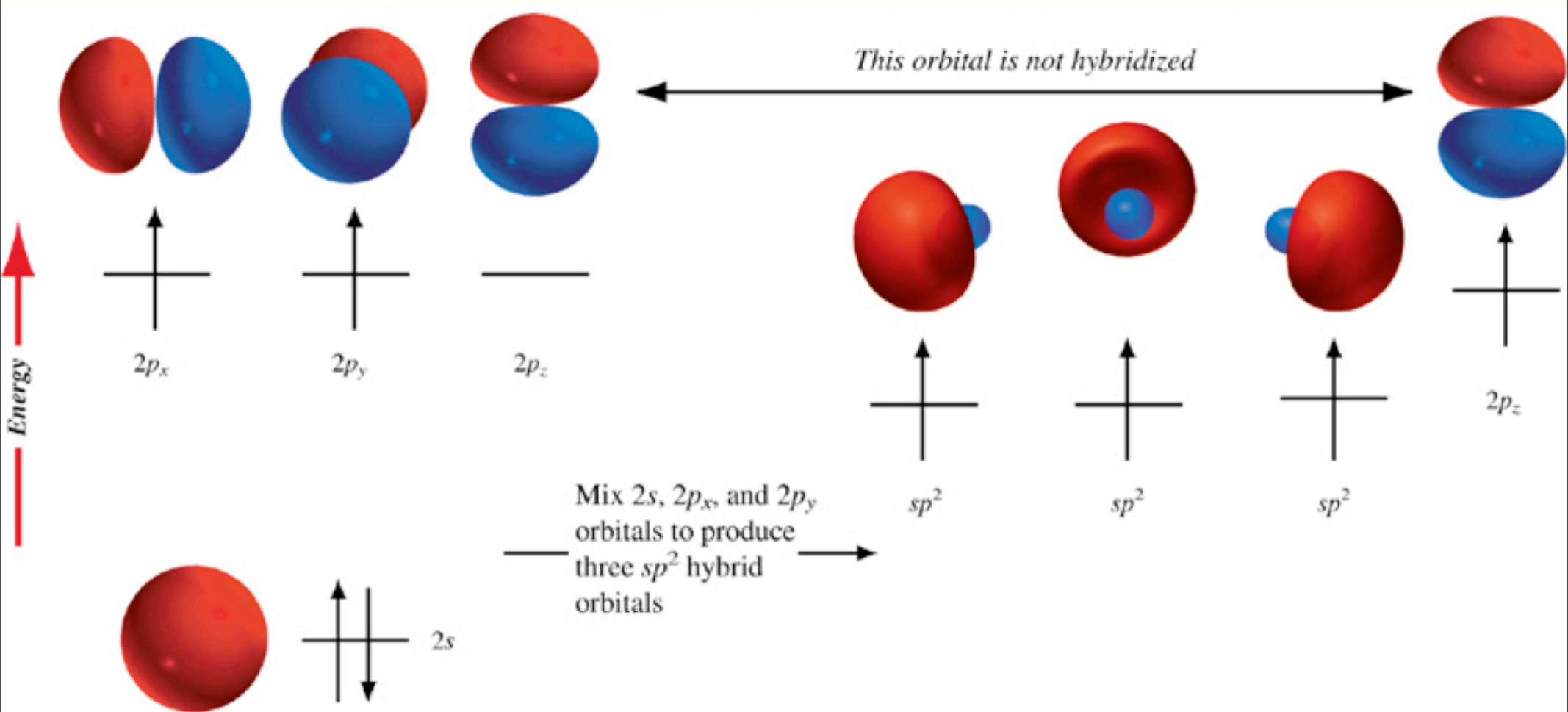
(a)



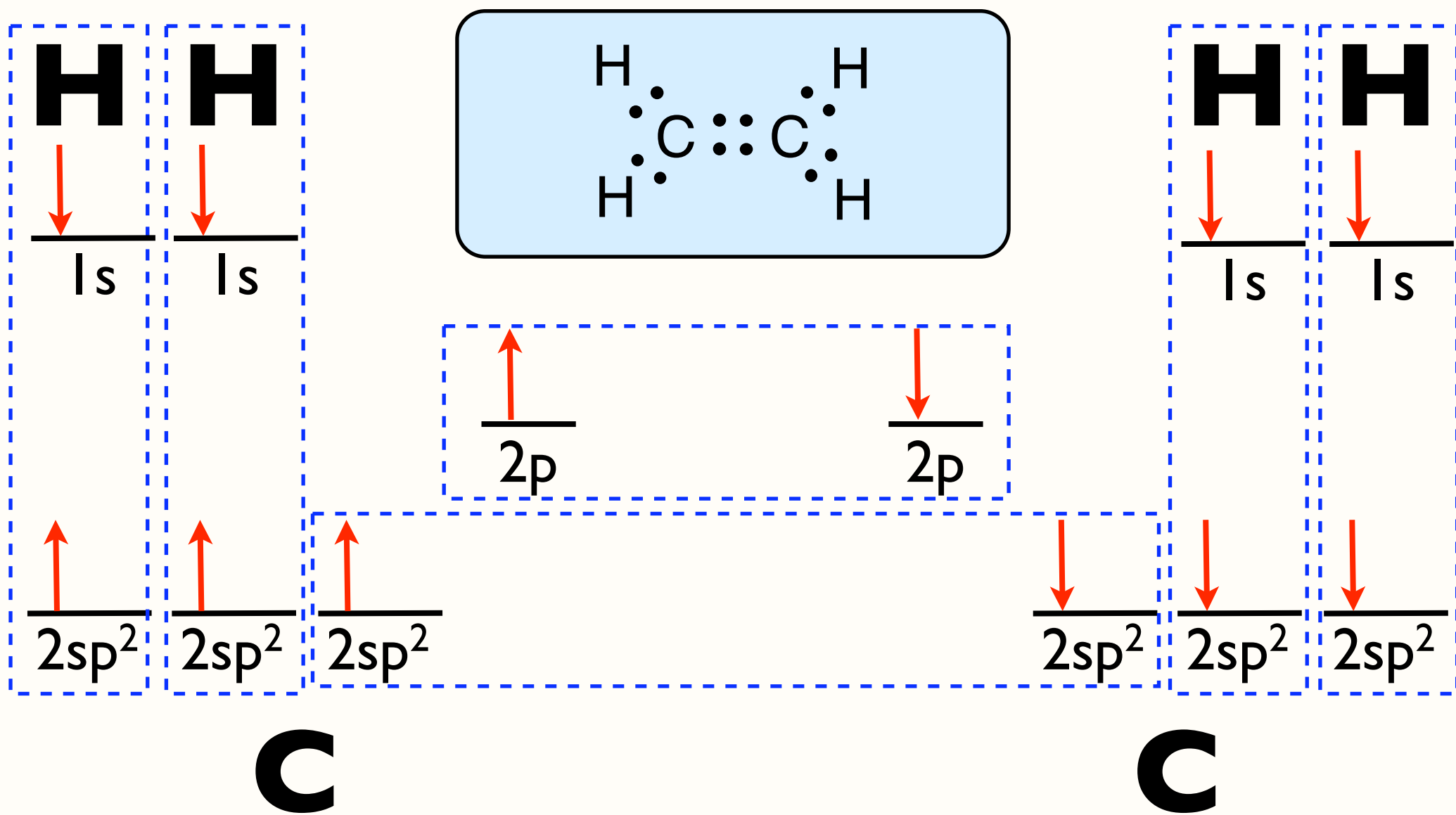
(b)

sp^2 Hybridization

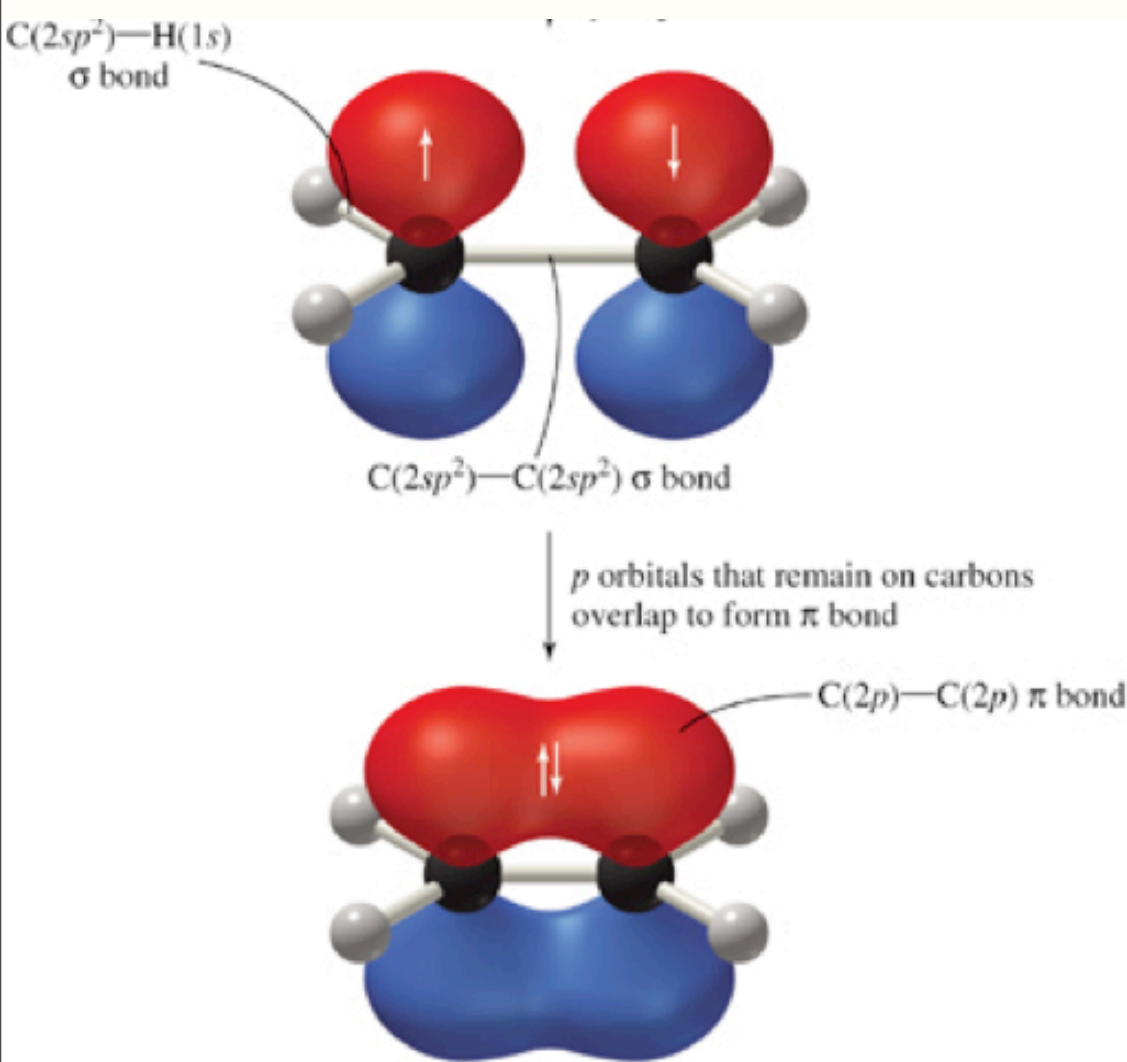
One p-orbital is Reserved—Not Hybridized



Valence Model of Bonding in Ethylene (with Hybridization)



Double Bond: 1 Pi-Bond & 1 Sigma-Bond

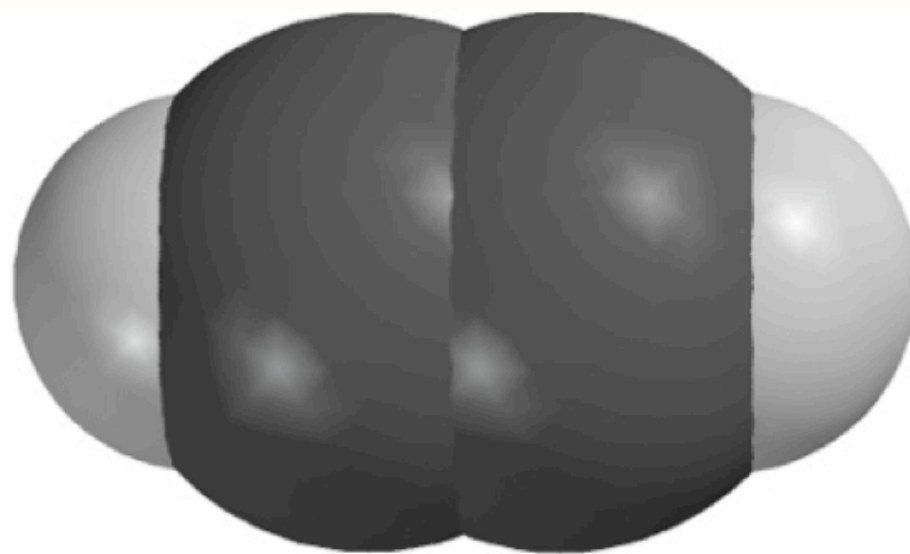
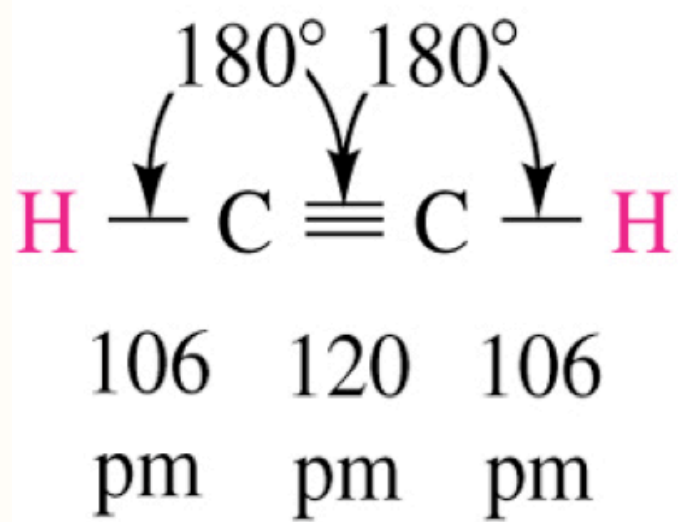


A double bond is formed by two orbital overlaps

1 pi (π) bond: side-to-side overlap of two p-orbitals; 2 π -electrons

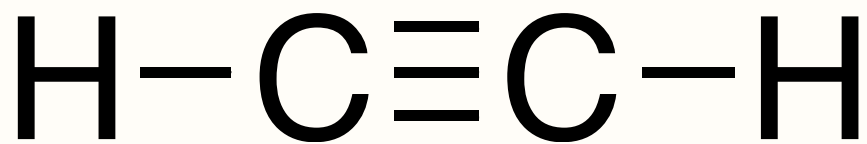
1 sigma (σ) bond: head-to-head overlap of two sp^2 -orbitals (not shown in figure on left)

Acetylenes



Self Test Question

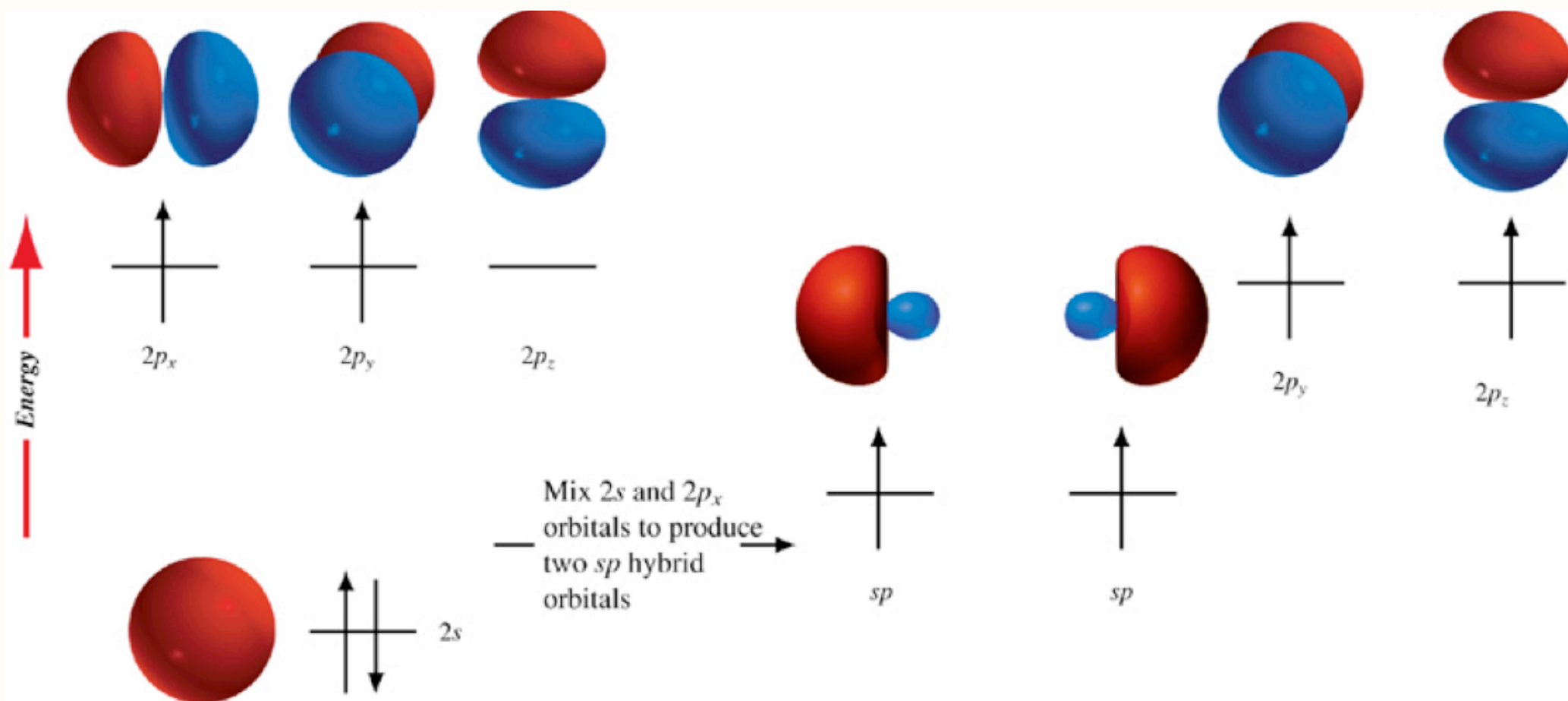
If the carbon atoms in acetylene are sp hybridized, what set of valence orbitals does each carbon atom contain?



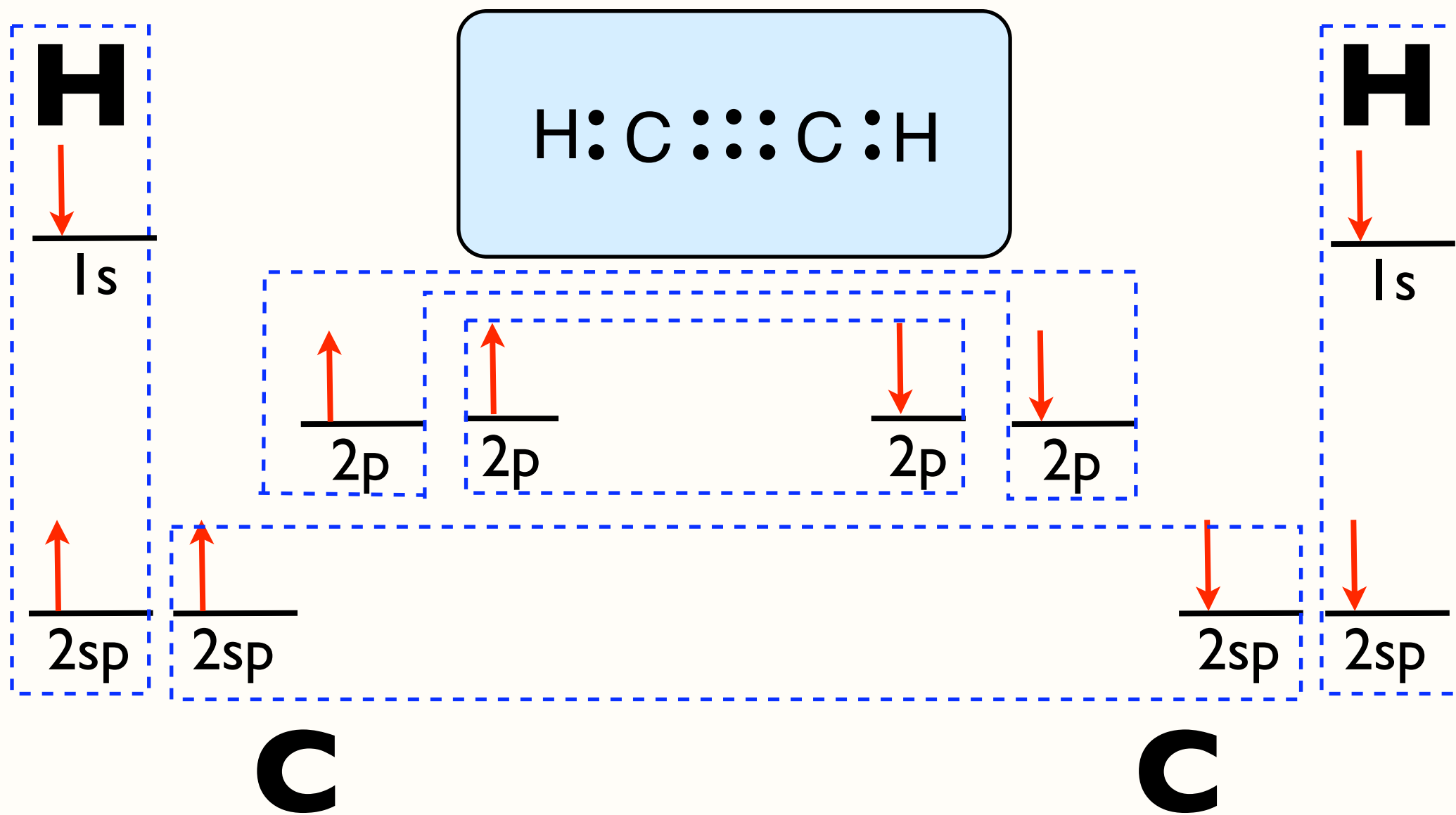
- A. one $2s$, three $2p$
- B. one $2s$, two $2p$, one sp
- C. two sp , two p , one sp^2
- D. three sp , one p
- E. two sp , two p

Hybridization in Acetylene

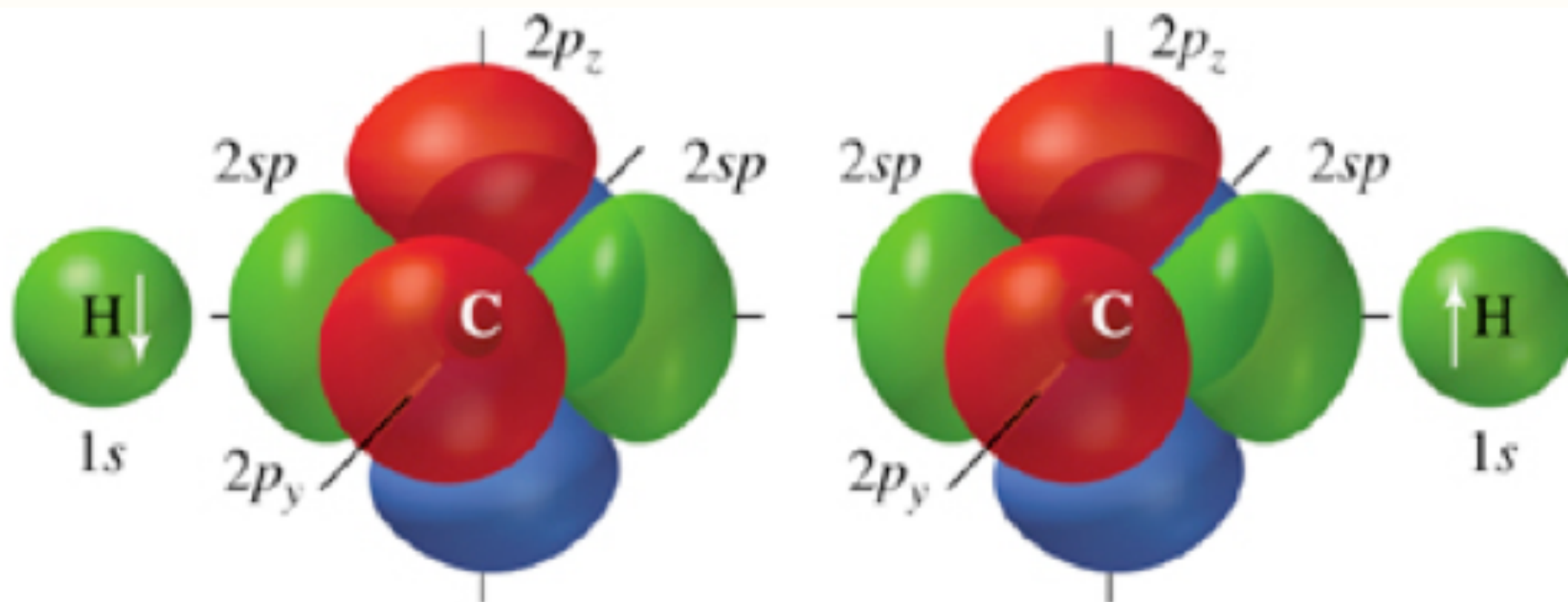
Two p-orbitals are Reserved—Not Hybridized



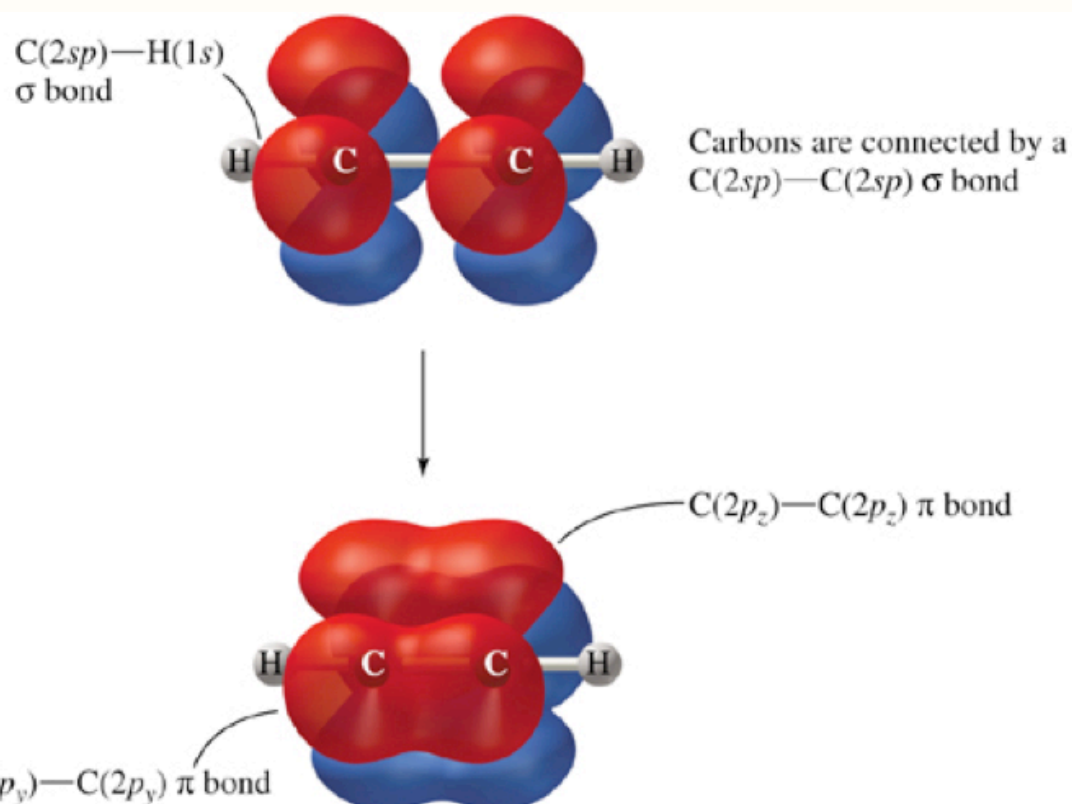
Valence Model of Bonding in Acetylene (with Hybridization)



Orbitals on sp -Hybridized Carbons



Triple Bond: 2 pi-bonds & 1 sigma-bond

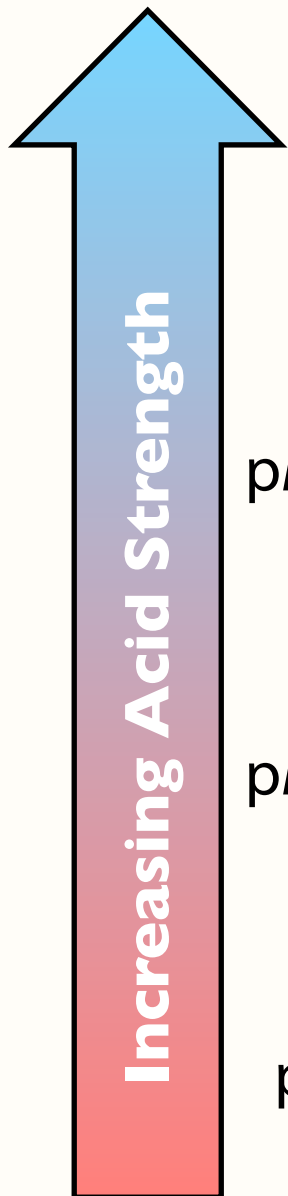


A triple bond is formed by three orbital overlaps

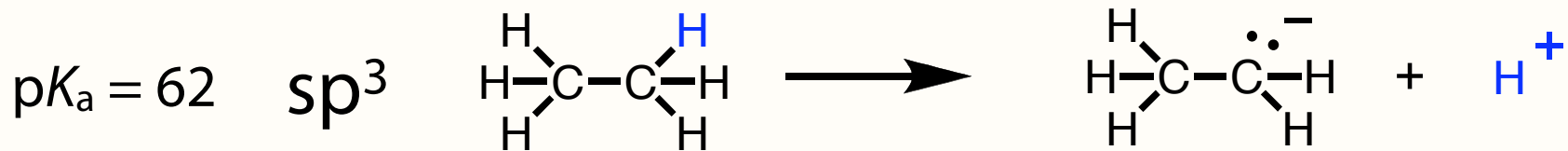
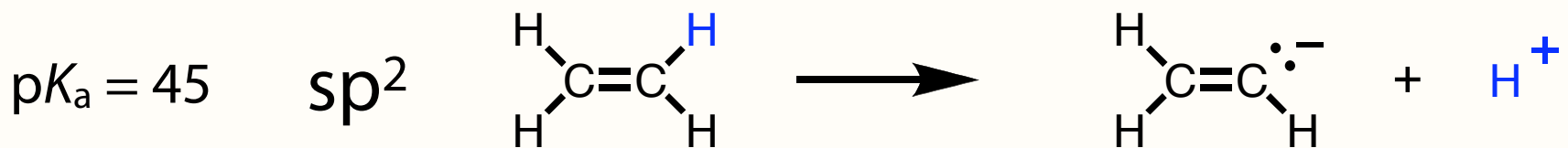
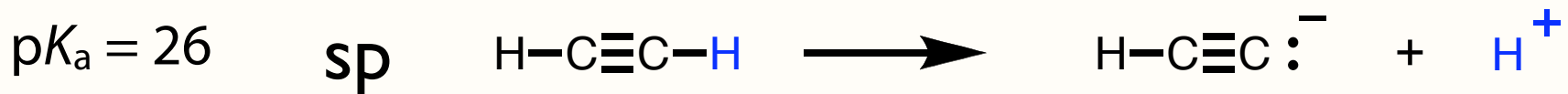
2 pi (π) bonds: side-to-side overlap of two sets of p-orbitals; 4 π -electrons

1 sigma (σ) bond: head-to-head overlap of two sp^2 -orbitals

Hybridization and Acidity



increased s-character =
increased electronegativity of carbon =
electrons closer to the nucleus =
stronger acid



Next Lecture...

Chapter 3: Sections 3.1-3.8

Molecule of the Week...2,4,6-Tribromoanisole

The Smell of Unintended Consequences

Johnson & Johnson Widens Recall of Smelly Over-the-Counter Drugs

By THE ASSOCIATED PRESS
Published: January 15, 2010

The health care giant [Johnson & Johnson](#) expanded a recall of over-the-counter medications on Friday, the second time it had done so in less than a month because of a moldy smell that has made users sick.

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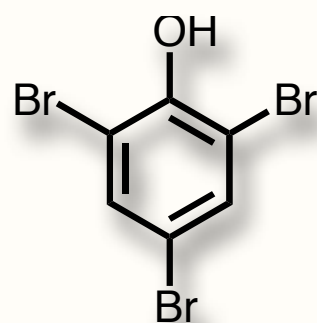
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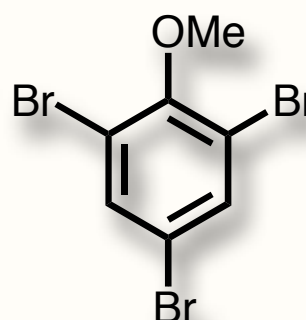
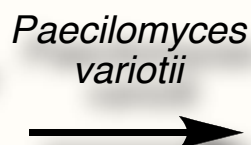
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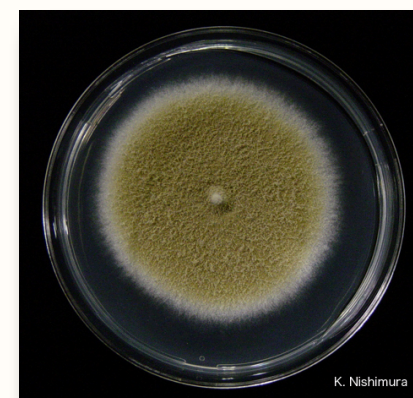
[Read more about tribromoanisole...](#)



2,4,6-Tribromophenol



2,4,6-Tribromoanisole



Paecilomyces variotii

Johnson & Johnson, the makers of Tylenol, have recently recalled millions of bottles of their over-the-counter medications as a result of a moldy smell, which has sickened several of their customers. An investigation by the FDA has concluded that the most probable root cause of this odor was the exposure of drug product bottles to wood pallets chemically treated with the chemical fungicide 2,4,6-tribromophenol (TBP). Unfortunately, the common fungus *Paecilomyces variotii* can convert TBP to its musty-smelling metabolite, 2,4,6-tribromoanisole, through methylation of the phenol functional group. A study on sultanas published in the *Journal of Agricultural and Food Chemistry* [1997, 45, 889] notes that, 2,4,6-tribromoanisole is high on the list of probable mustiness causing agents that taint packaged foods.