Cornell University

Carbocation Stability, Alkene Stability, Acid & Base Stability, and Boiling Points

Brendan Parent & Auriole C.R. Fassinou

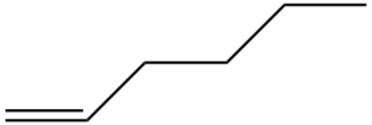
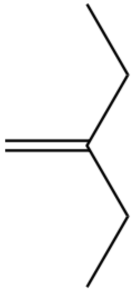
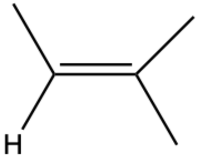
July 03rd, 2020

OCSP Lecture #6

Lecture 6 Learning Objectives

- Ranking Alkene Stability
  - Primary, Secondary, Tertiary, and Quaternary Alkenes
- Ranking Carbocation Stability
  - Primary, Secondary, and Tertiary Carbocations
  - The Hyperconjugation Explanation of Stability
  - Hydride Shifts
  - Methyl Shifts
- Ranking Bronsted Acid-Base Stability
  - Periodic Trends (EN and Size), Resonance Effects, and Polar Inductive Effect of Substituents
- Comparing Boiling Points
  - Intermolecular Forces (Ionic, Hydrogen Bonding, Dipole-Dipole, Van der Waals)
  - Carbon Chain Length
  - Molecule Branching

Alkene Stability

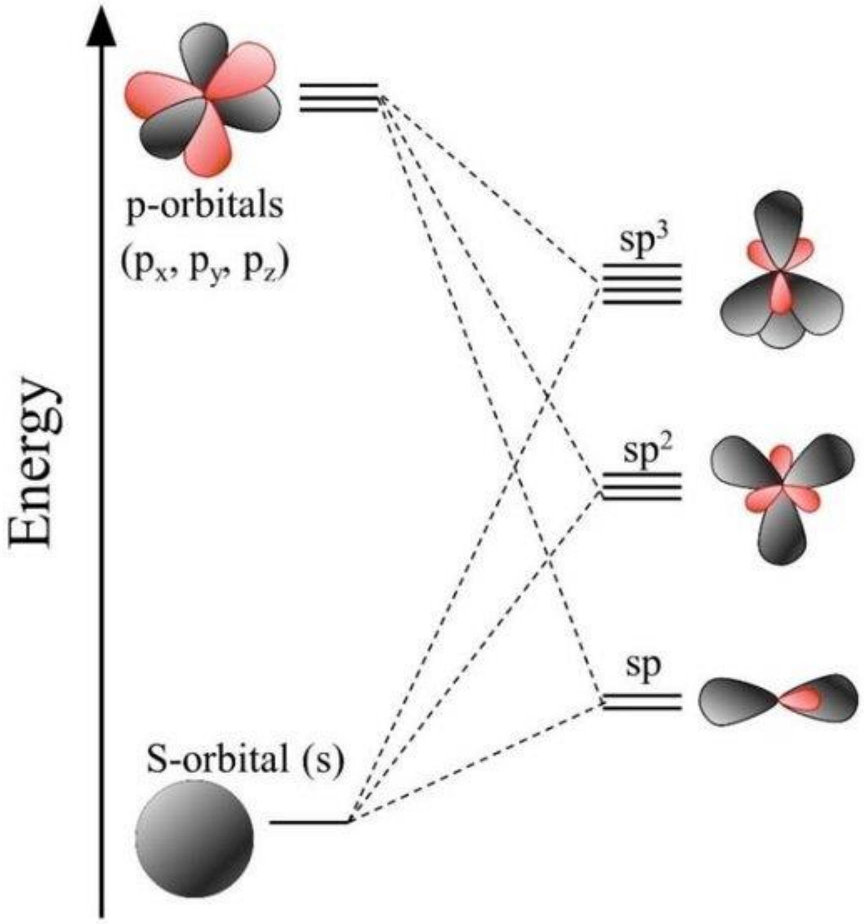
Alkene	# of attached alkyl groups	ΔH_f°
	1	-40.5 kJ/mol
	2	-55.8 kJ/mol
	3	-62.7 kJ/mol

Alkene Stability

Stability increases with increasing number of alkyl groups attached at the double bond

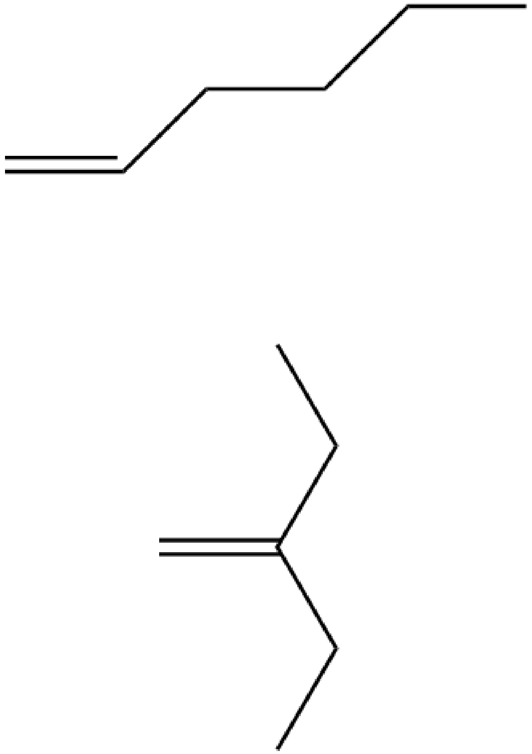
Why?

Hybridization



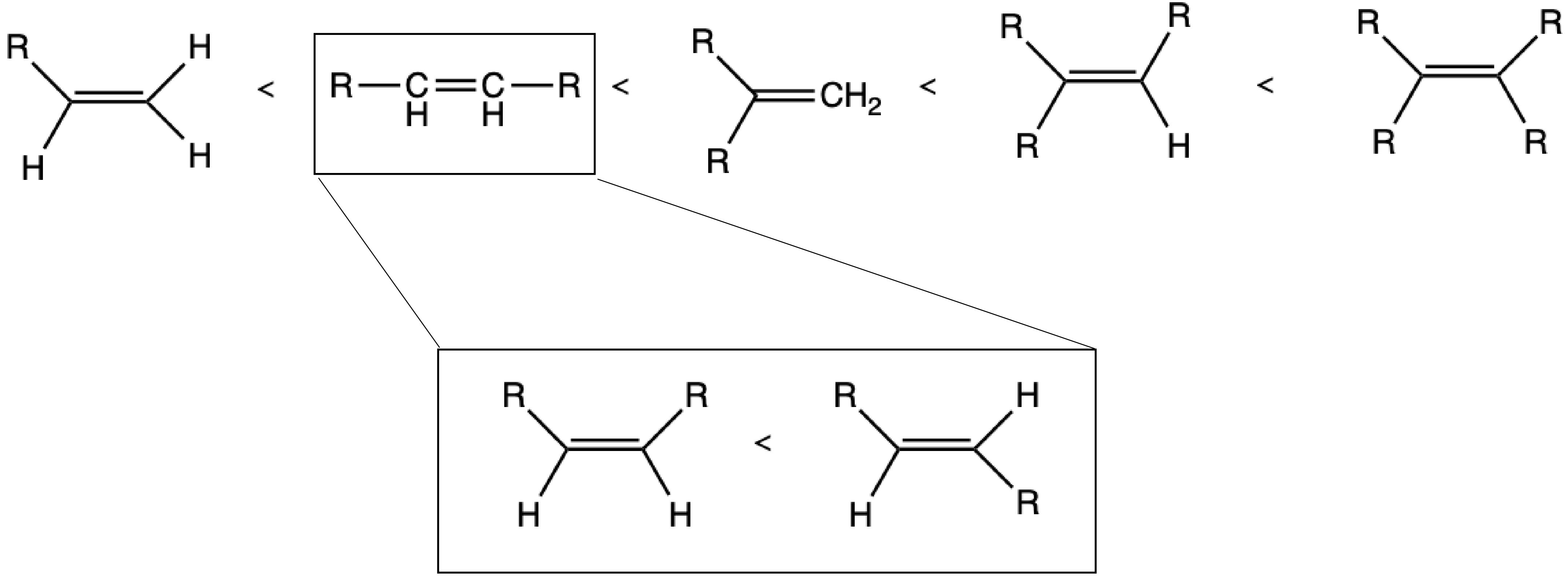
Jafari, Mohammad. (2017). Application of Vibrational Spectroscopy in Organic Electronics.

Molecule Comparison



Increasing number of Csp2 – Csp3 bonds leads to increased stability

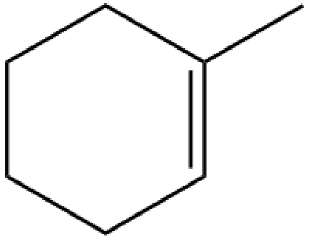
General Order of Stability

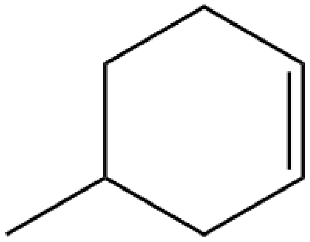


Practice Problems

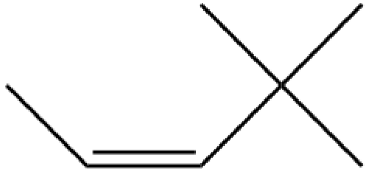
Within each series, arrange the compounds in order of **increasing** stability.

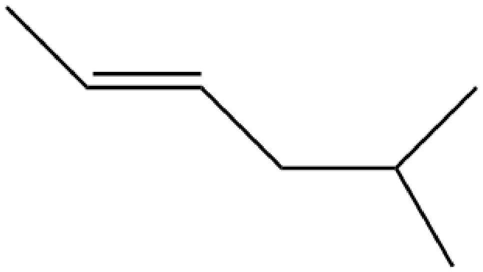
a)



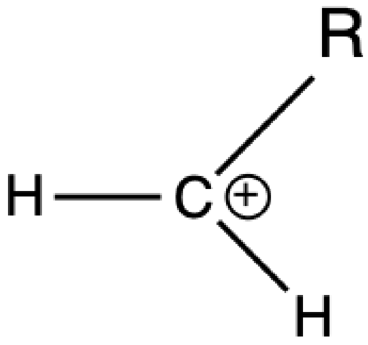


b)



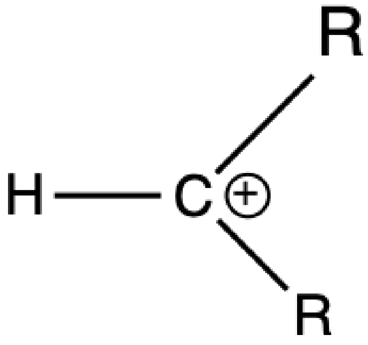


Carbocation Stability



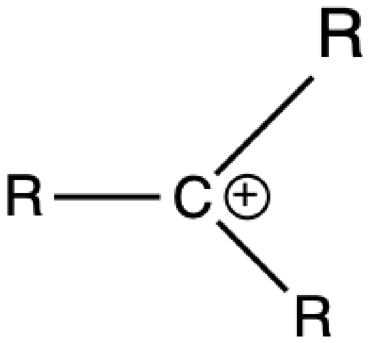
1° Carbocation

<



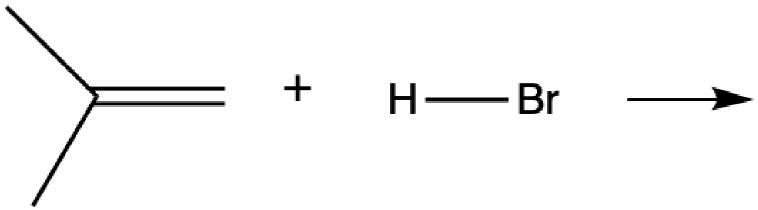
2° Carbocation

<

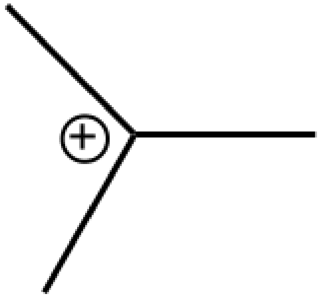


3° Carbocation

Reactions Involving Carbocations



Closer Look



$CH_3CH_2CH_2\overset{\oplus}{C}H_2$

Why are tertiary carbocations so much more stable?

Hyperconjugation

Stabilizing Carbocations

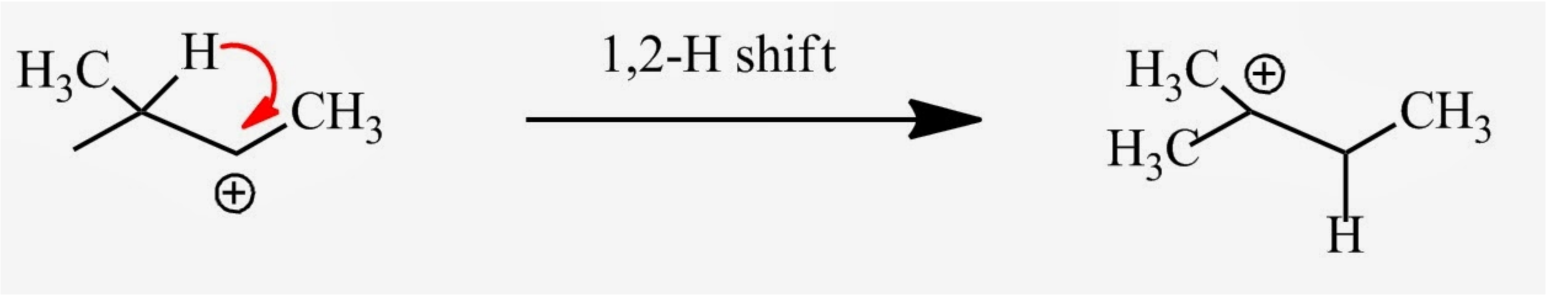
- In order to stabilize carbocations, molecules can undergo changes (**known as hydride and methyl shifts**) that bring forth a more stable carbocation. These hydride + methyl shifts occur through the movement of electrons into the empty p-orbitals of the carbocation.

Example of A Hydride Shift…

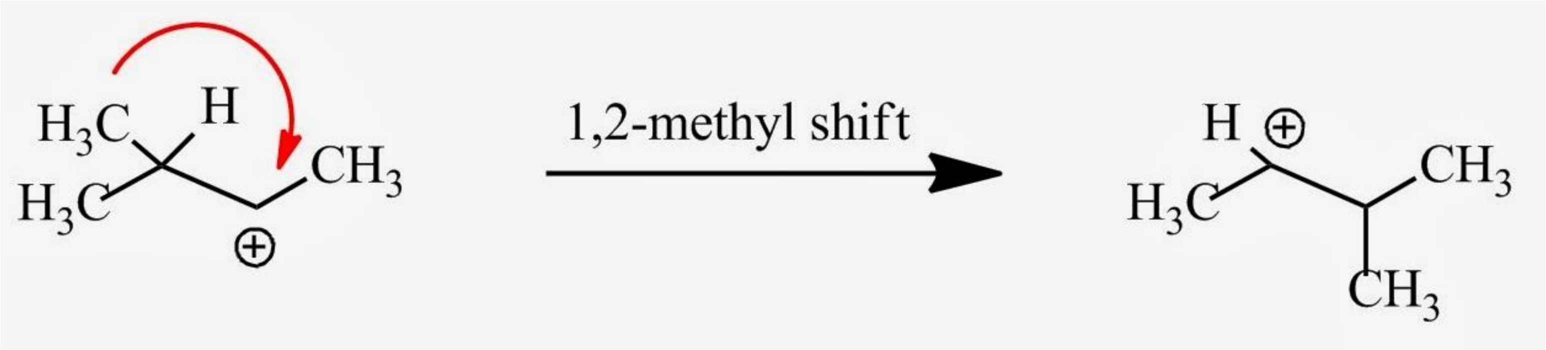
Example of A Methyl Shift…

Making Carbocations More Stable (Summarized)

- Hydride Shifts



- Methyl Shifts



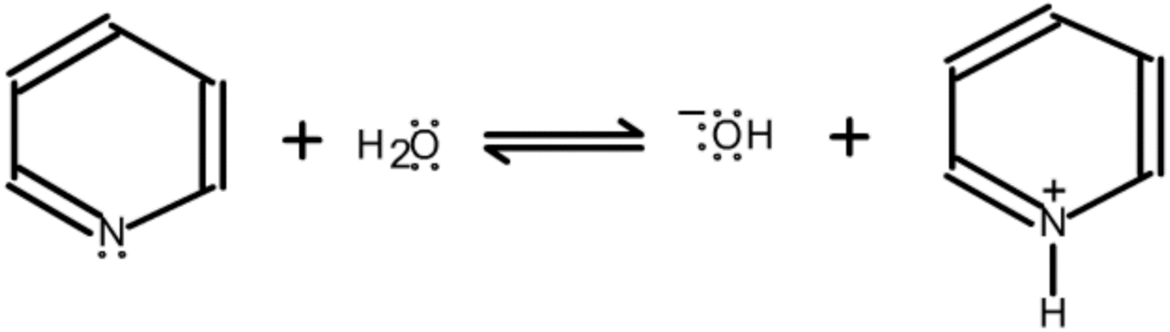
Lecture 6 Learning Objectives

- Ranking Alkene Stability
  - Primary, Secondary, Tertiary, and Quaternary Alkenes
- Ranking Carbocation Stability
  - Primary, Secondary, and Tertiary Carbocations
  - The Hyperconjugation Explanation of Stability
  - Methyl Shifts
  - Hydride Shifts
- Ranking Bronsted Acid & Base Stability
  - Periodic Trends, Resonance Effects, and Polar Inductive Effect of Substituents
- Comparing Boiling Points
  - Intermolecular Forces (Ionic, Hydrogen Bonding, Dipole-Dipole, Van der Waals)
  - Carbon Chain Length
  - Molecule Branching

Practice Problem (Review Bronsted-Lowry)

Label each reactant and product in these two reactions as a Bronsted Acid or Base.

$$HCN + NH_2^- \rightleftharpoons CN^- + NH_3$$



Using the Bronsted theory, classify the following as either an acid or a base.

$CH_3CH_2O^-$, $CH_3CH_2NH_3^+$, C_6H_5OH, $C_5H_6N^+$, H_2O, OH^-, C_5H_5N

Let’s Review Bronsted-Lowry Acids and Bases…

- Acidity can be assessed by the presence of factors that stabilize the conjugate base.
    - These factors are… Electronegativity, Size, Resonance, & Polar Induction

Electronegativity Trends

1. Electronegativity: When comparing atoms within the same row of the periodic table, the more EN the anionic atom in the conjugate base, the better it is at accepting the negative charge.

Size Trends

2. Size: When comparing atoms within the same group of the periodic table, the easier it is for the conjugate base to accommodate negative charge (lower charge density). <u>This trend only works within groups!</u>

Resonance Effect

- Resonance: In the carboxylate ion, the negative charge is delocalized across 2 EN atoms which makes it more stable than being localized on a specific atom as in the alkoxide.

Polar Inductive Effect

- Polar Induction: The presence of EN atoms increases the acidity by inducing electron density towards itself.

Practice Problem

- Place the following compounds in order of acidity (from least acidic to most acidic).

$R-H$

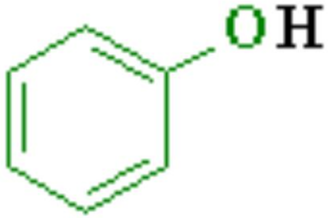
alkanes

$R-OH$

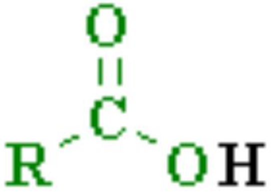
alcohols

$R-NH_2$

amines



phenols

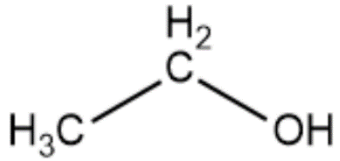


$R-C(=O)-OH$

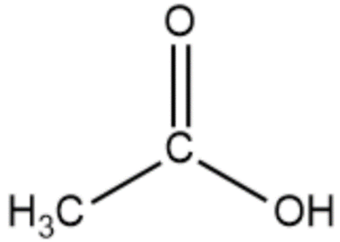
carboxylic acids

Practice Problem

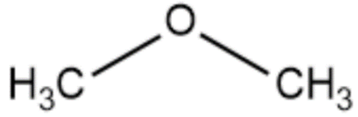
- Place the following compounds in order of acidity (from least acidic to most acidic).



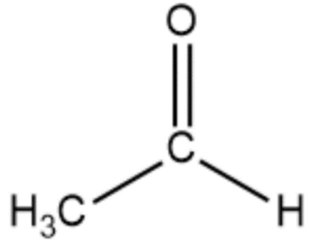
1



2



3



4

Bronsted-Lowry Bases…

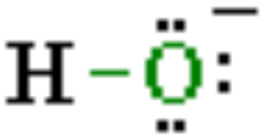
- A convenient way to look at basicity is based on electron pair availability, the more readily they can be donated to form a new bond to a proton, the stronger the base.

Electron Pair Availability

- Electronegativity: When comparing atoms within the same row of the Periodic Table, the more EN the atom donating electrons is, the weaker the base.
- Size: When comparing atoms within the same group of the Periodic Table, the larger the atom, the weaker the base.
- Resonance: The greater the stabilization of the lone pairs, the weaker the base

Practice Problem

- Place the following compounds in order of basicity (from least basic to most basic).



alkoxides

amines

amide ions