Problem Set #3
Due: March 3, 4:00 pm

1. Calculate the degree of unsaturation for C₈H₁₀F₃NO.
   If fully saturated: C₈H₁₈
   \[(\text{F}) (\text{N})\]
   \[18 \text{H} - (10\text{H} + 3 - 1) = \frac{\text{C}_8\text{H}_2}{2} - 3 \text{H}_2 = \boxed{3}\]

2. Assign E-Z configuration to each alkene.

   \[\text{E} \quad \text{Z}\]

3. Name the following alkenes.
   \[\text{cis-5-methyl-2-heptene}\]
   \[\text{1-isopropyl-3-methylcyclohexene}\]
   \[4\text{-butyl-5-methyl-1,4-hexadiene}\]
4. For each of the following reactions, label the type of nucleophile: lone pair (n), pi bond (\(\pi\)), sigma bond (\(\sigma\)), and the type of electrophile: empty atomic orbital (a), polarized pi bond (\(\pi^*\)), polarized sigma bond (\(\sigma^*\)). Draw in all lone pairs and use curved arrows to show how the nucleophile attacks the electrophile and show the product of these one-step reactions.

a) 

b) 

c) 

d) 

e) 

f) 

g) Show the initial orbital overlap for reaction f.
5. The equilibrium constant for the ring-inversion of fluorocyclohexane is 1.5 at 25 °C. Calculate the fraction of the axial conformer at this temperature.

a) Draw fluorocyclohexane and its ring-flipped conformer.

\[
\begin{align*}
\text{F} & \quad \Rightarrow \quad K_{eq} = 1.5 \\
\text{F} & \quad \Rightarrow \quad \text{F}
\end{align*}
\]

b) Write the equilibrium equation.

\[
K_{eq} = \frac{[\text{equatorial}]}{[\text{axial}]}
\]

c) Solve for the percentage of axial conformer at equilibrium.

\[
\% \text{ axial} = \frac{[\text{axial}]}{[\text{axial}] + [\text{equatorial}]}
\]

\[
\begin{align*}
&= \frac{[\text{axial}]}{[\text{axial}] + K_{eq}[\text{axial}]} \\
&= \frac{[\text{axial}]}{[\text{axial}](1 + K_{eq})} \\
&= \frac{1}{1 + K_{eq}} = \frac{1}{1 + 1.5} = \frac{1}{2.5} = 40\%
\end{align*}
\]
6. Calculate $\Delta H$ for each of the following reactions. (See the table at the end of this problem set).

a) $\text{CH}_3\text{CH}_2\text{Cl} + \text{HI} \to \text{CH}_3\text{CH}_2\text{I} + \text{HCl}$

\[
\begin{array}{c|cc|c}
\text{Bonds Broken} & \text{kcal/mol} & \text{Bonds Formed} & \text{kcal/mol} \\
\hline
\text{CH}_3\text{CH}_2 - \text{Cl} & 81.5 & \text{CH}_3\text{CH}_2 - \text{I} & 53.5 \\
\text{H - I} & 71.3 & \text{H - Cl} & 10.3 \\
\hline
& 152.8 & & 153.8 \text{ kcal/mol}
\end{array}
\]

$\Delta H = 152.8 - 153.8 = -1.0 \text{ kcal/mol}$

b) $\text{CH}_3\text{CH}_2\text{OH} + \text{HBr} \to \text{CH}_3\text{CH}_2\text{Br} + \text{H}_2\text{O}$

\[
\begin{array}{c|cc|c}
\text{Bonds Broken} & \text{kcal/mol} & \text{Bonds Formed} & \text{kcal/mol} \\
\hline
\text{CH}_3\text{CH}_2 - \text{OH} & 91.5 & \text{CH}_3\text{CH}_2 - \text{Br} & 69 \\
\text{H - Br} & 87.5 & \text{H - OH} & 119 \\
\hline
& 179 & & 188
\end{array}
\]

$\Delta H = 179 - 188 = -9.0 \text{ kcal/mol}$
7. a) Draw an energy diagram for a two-step reaction passing through an intermediate that is less stable than both the starting material and the product, where the product is more stable than the starting material and the activation energy for proceeding from the intermediate to the product is higher than that for proceeding from the intermediate to the starting material.

![Energy Diagram](image)

b) Which species does the first transition state resemble more closely (circle one)?

- starting material
- intermediate

(c) Which species does the second transition state resemble more closely (circle one)?

- product
- intermediate

d) Which transition state is involved in the rate determining step of the overall reaction (circle one)?

- first
- second

e) The reaction is: 

- exergonic
- endergonic

f) ΔG is: 

- positive
- negative

g) \( K_{eq} \) is:

- >1
- <1
- 0
8. Consider the following reaction.

a) Show the product (ignore stereochemistry).

\[
\text{CH}_3 - \text{CH}_3 + \text{H-Cl} \rightarrow \text{CH}_3 - \text{CH}_3
\]

b) How many stereoisomers will form during this reaction?

- 2 chirality centers
- \(2^2 = 4\) stereoisomers

c) Show the mechanism for arriving at each of the stereoisomers.

\[
\text{CH}_3 - \text{CH}_3 + \text{H-Cl} \rightarrow \text{enantiomers} + 4 \text{ sets of diastereomers}
\]

d) Label the relationships between the stereoisomers.

e) The products are (circle one): optically active or optically inactive.
9. Reaction b proceeds $2.5 \times 10^8$ times faster than reaction a. Explain with mechanisms and reaction coordinate diagrams.

\[
\text{a) } \quad \begin{array}{c}
\text{H}_3\text{C} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\hline
\text{H} - \text{Br} \\
\text{H} \\
\end{array} \quad + \quad \begin{array}{c}
\text{H} - \text{Br} \\
\text{H} \\
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{H}_3\text{C} - \text{C} - \text{CH}_3 \\
\text{H} \\
\end{array}
\]

\[
\text{b) } \quad \begin{array}{c}
\text{H}_3\text{CO} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\hline
\text{H} - \text{Br} \\
\text{H} \\
\end{array} \quad + \quad \begin{array}{c}
\text{H} - \text{Br} \\
\text{H} \\
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{H}_3\text{CO} - \text{C} - \text{CH}_3 \\
\text{H} \\
\end{array}
\]

\[
\text{a) } \quad \begin{array}{c}
\text{H}_3\text{C} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\hline
\text{H} - \text{Br} \\
\text{H} \\
\end{array} \quad \xrightarrow{+\text{H}^+} \quad \begin{array}{c}
\text{H}_3\text{C} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\hline
\text{H} - \text{Br} \\
\text{H} \\
\end{array} \quad + \quad \begin{array}{c}
\text{Br}^- \\
\text{H} \\
\end{array}
\]

\[
\text{b) } \quad \begin{array}{c}
\text{H}_3\text{CO} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\hline
\text{H} - \text{Br} \\
\text{H} \\
\end{array} \quad \xrightarrow{+\text{H}^+} \quad \begin{array}{c}
\text{H}_3\text{CO} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\hline
\text{H} - \text{Br} \\
\text{H} \\
\end{array} \quad + \quad \begin{array}{c}
\text{Br}^- \\
\text{H} \\
\end{array}
\]

The intermediate of reaction b is resonance stabilized, + lower in energy than the intermediate of reaction a. Formalin of the intermediate is endo/thermic process. Thus, the structure of the TS resembles the structure of the intermediate. Because the intermediate of b is lower in energy than a, the transition state of b is also lower in energy. Therefore, reaction b has a smaller ΔG‡ and occurs faster.
10. Show the mechanism for each reaction.

a) \[
\begin{align*}
\text{Cycloalkene} + \text{H}^+ X^- & \rightarrow \text{Cycloalkane} \\
\text{Cycloalkene}^+ + \text{X}^- & \rightarrow \text{Cycloalkane}^+ + \text{X}^-
\end{align*}
\]

Hydride shift: 2º to 3º carbocation

b) \[
\begin{align*}
\text{Cycloalkene} + \text{H}^+ X^- & \rightarrow \text{Cycloalkane} \\
\text{Cycloalkene}^+ + \text{X}^- & \rightarrow \text{Cycloalkane}^+ + \text{X}^-
\end{align*}
\]

Methyl shift: 2º to 3º carbocation
c) \[ \text{cyclohexene} + H-X \rightarrow \text{cyclopentadiene} \]
\[ \text{cyclopentadiene} + X^{-} \rightarrow \text{cyclopentadienyl cation} + X^{-} \]
ring expansion 4 (strained) to 5 carbon ring

\[ \text{d) cyclopropene} + H-X \rightarrow \text{cyclohexene} \]
\[ \text{cyclohexene} + X^{-} \rightarrow \text{cyclohexadienyl cation} + X^{-} \]
4 (strained) to 5 carbon ring expansion
Table 2.8 Bond Dissociation Energies and Average Bond Energies for Various Types of Bonds

<table>
<thead>
<tr>
<th>Bond</th>
<th>Energy</th>
<th>Bond</th>
<th>Energy</th>
<th>Bond</th>
<th>Energy</th>
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<td>F—I</td>
<td>58</td>
<td>H—Br</td>
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<td>I—I</td>
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Polyatomic Molecules

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<tr>
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<td>CH₃CH₂—CHCH₂</td>
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<td>H—CH₂CH₃</td>
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Table 2.8 (Continued)

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<td>( \text{H}_2\text{N} \equiv \text{C}_6\text{H}_5 )</td>
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<td>( \text{H}_2\text{N} \equiv \text{COCH}_3 )</td>
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<td>( \text{O}_2\text{N} \equiv \text{NO}_2 )</td>
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<td>( \text{O}_2\text{N} \equiv \text{COCH}_3 )</td>
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<th>Energy</th>
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<td>72 [301]</td>
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<tr>
<td>( \text{CH}_3 \equiv \text{CH}_2\text{CHCH}_2 )</td>
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## Multiple Bonds

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<tbody>
<tr>
<td>( \text{O} \equiv \text{O} )</td>
<td>119 [498]</td>
<td>( \text{CF}_2 \equiv \text{CF}_2 )</td>
<td>76.3 [319]</td>
</tr>
<tr>
<td>( \text{O} \equiv \text{CO} )</td>
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<td>( \text{CH}_2 \equiv \text{NH} )</td>
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<td>( \text{O} \equiv \text{CH}_2 )</td>
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<td>( \text{C} \equiv \text{O} )</td>
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<td>( \text{N} \equiv \text{N} )</td>
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<td>( \text{HN} \equiv \text{NH} )</td>
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<td>( \text{N} \equiv \text{CH} )</td>
<td>224 [937]</td>
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<td>( \text{CH}_2 \equiv \text{CH}_2 )</td>
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<td>( \text{HC} \equiv \text{CH} )</td>
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## Representative Average Bond Energies

### Single Bonds

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<th>Si</th>
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<td>60 [251]</td>
<td>67 [280]</td>
<td>141 [586]</td>
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<td>53 [222]</td>
<td>50 [209]</td>
<td>96 [402]</td>
<td></td>
<td></td>
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<tr>
<td>43 [180]</td>
<td>69 [289]</td>
<td></td>
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<td></td>
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<td>50 [209]</td>
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<td>45 [188]</td>
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## Multiple Bonds

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<th>Triple bond</th>
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<td>96 [402]</td>
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<tr>
<td>( \text{N} \equiv \text{N} )</td>
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<td>100 [418]</td>
<td>226 [946]</td>
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<td>148 [619]</td>
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<td>69 [289]</td>
<td>148 [619]</td>
<td>213 [891]</td>
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</table>


*In kcal mol\(^{-1}\). Numbers in brackets are values in kJ mol\(^{-1}\).


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Guide to the

1. \( \Delta H^\circ \) of Benson's gas phase; almost always even better.

2. In arbitrary valence bond scheme, \( \Delta H^\circ \) of the bond affect important colinear enthalpies.