Chemistry 21 Problem Set

A. Alkenes and Reactivity

1. Draw structures for the following:
   a) vinyl alcohol
      \[
      \text{\begin{center}
      \includegraphics[width=0.5\textwidth]{vinyl_alcohol.png}
      \end{center}}
   \]

   b) diallyl ether
      \[
      \text{\begin{center}
      \includegraphics[width=0.5\textwidth]{diallyl_ether.png}
      \end{center}}
   \]

   c) (2E, 4E)-1-chloro-3-methyl-2,4-hexadiene
      \[
      \text{\begin{center}
      \includegraphics[width=0.5\textwidth]{2E_4E.png}
      \end{center}}
   \]

   d) (2Z, 4E)-1-chloro-3-methyl-2,4-hexadiene
      \[
      \text{\begin{center}
      \includegraphics[width=0.5\textwidth]{2Z_4E.png}
      \end{center}}
   \]

   e) (2Z, 4Z)-1-chloro-3-methyl-2,4-hexadiene
      \[
      \text{\begin{center}
      \includegraphics[width=0.5\textwidth]{2Z_4Z.png}
      \end{center}}
   \]

2. What is the equation that describes the relationship between \( \Delta G, \Delta H, \Delta S, \) and \( T \)?
   \[
   \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ
   \]

3. What is the equation that describes the relationship between \( \Delta G \) and \( K_{eq} \)?
   \[
   \Delta G_{rxn} = -RT \ln K_{eq}
   \]

4. What does \( K_{eq} \) measure?
   \[
   K_{eq} = \frac{[\text{products}]}{[\text{reactants}]} \text{ at equilibrium}
   \]

5. What are the components of a reaction that affect the rate of a reaction?
   Consider the reaction coordinates shown for the reaction \( SM \rightarrow P \)
   a) Determine the rate limiting step.
      \( SM \rightarrow I \)
   b) Which is the more stable TS?
      \( TS_2 \)
   c) Which step (\( SM \rightarrow I \) or \( I \rightarrow P \)) in the mechanism is faster?
      \( I \rightarrow P \)
   d) Is the reaction endergonic or exergonic?
      \( \text{exergonic} \)
B. Reactions of Alkenes

1. Generate a list of some nucleophiles and electrophiles. What are the common features of nucleophiles? of electrophiles?

   \[ \text{Nu} = e^- \text{ available to attach e-deficient site i.e. } \text{H}_2\text{O}, \text{ROH}, \text{OH}^-, \text{OR}^-, \text{X}^- \text{H}_2^+ \text{ and } \text{π}^- \]

   \[ \text{E} = \text{ formal or partial } \Theta \text{ charge i.e. } \text{H}_2\text{O}^+ (\text{H}^+) \text{ carbocations, carbonyl C, BH}_3 \]

2. Predict the major product(s) generated when 3-methylcyclohexene reacts with:
   (You don’t need to indicate stereochemistry in this exercise.)

   a) HCl
   \[ \text{Cl} \]

   b) CH₃COOOH
   \[ \text{O} \]

   c) H₂O, and a trace amount of H₂SO₄
   \[ \text{OH} \]

   d) CH₂N₂ and heat
   \[ \text{O} \]

3. Predict the major product(s) generated when 8-methylcyclohexene reacts with:
   (You don’t need to indicate stereochemistry in this exercise.)

   a) 1. BH₃/THF  2. H₂O₂/ OH⁻
   \[ \text{OH} \]

   b) 1. Hg(OAc)₂, CH₃CH₂OH  2. NaBH₄
   \[ \text{OH} \]

   c) H₂ / Pd / C
   \[ \text{O} \]

   d) Br₂, H₂O, NaCl
   \[ \text{Br}^- \]
4. Propose a mechanism for the reaction:

$$3\text{-cyclopropylpropene} + H_2O \text{ (in acid)} \rightarrow 1\text{-methylcyclobutanol}$$

C. Stereoisomerism

1. What are the features of:
   a) a stereocenter. Give an example.
   
   ![Four different substituents example]

   b) a chiral molecule. Give an example.
   
   ![An optically active molecule example]

   c) a pair of enantiomers. Give example.
   
   ![Non-superposable mirror images example]

   d) diastereomers. Give example.
   
   ![Stereoisomers that are not enantiomers example]

   e) meso compounds. Give an example.
   
   ![A compound with 2 or more stereocenters example]

2. Consider 2-chlorobutane.

   a) Illustrate the R and S enantiomers with perspective drawings.

   ![Perspective drawings example]

   b) Illustrate the R and S enantiomers with Newman projections.

   ![Newman projections example]

   c) Illustrate the R and S enantiomers with Fischer projections.

   ![Fischer projections example]
3. Optical Activity

a) Qualitatively describe optical activity.

The phenomenon whereby plane-polarized light rotates through interaction with overall chirality in a molecule

b) What equation describes the relationship between specific rotation and observed rotation?

\[
[\alpha]_n^T = \frac{\alpha_{\text{observed}}}{c (g/mL) \times l (dm)}
\]

c) How is enantiomeric excess measured?

relevent equation: \([\alpha]_n^T \times x + [\alpha]_n^T (1-x) = \alpha_{\text{observed}}

\[
x = \frac{\text{fraction of mix that is one enantiomer}}{\text{equal mix of enantiomers}}
\]

\[
y = (1-x) = \frac{\text{fraction of mix that is other enantiomer}}{\text{optically inactive}}
\]

d) What is meant by a racemic mixture?

4. Using Fischer projections, give the major products – include all stereoisomers as appropriate for reactions in which

a) (Z)-3,4-dimethyl-2-pentene is treated with the reagents listed. (i – v):

b) (E)-3,4-dimethyl-2-pentene is treated with the reagents listed. (i – v):

i. HBr

\[
CH(CH_3)_2
\]

a) \(CH_3 + Br\) and enantiomer

and b) \(CH_2CH_3\)

ii. Br_2, CH_2Cl_2

6. + Br

6. + Br

a) \(CH(CH_3)_2\)

b) \(CH(CH_3)_2\)

iii. Br_2, CH_3OH

6. + Br

6. + Br

a) \(CH(CH_3)_2\)

b) \(CH(CH_3)_2\)

iv. H^+, H_2O

6. + OH

6. + OH

a) and b) \(CH(CH_3)_2\)

b) \(CH(CH_3)_2\)

v. H_2, Pt/C

\[
CH(CH_3)_2
\]

\[
CH_3 + H + \text{enantiomer}
\]
c) (E)-3,4-dimethyl-3-hexene is treated with:

i) HBr

\[
\begin{align*}
\text{CH}_3 \text{CH}_2 & + \ell \text{ Br} \\
\text{CH}_3 \text{CH}_2 & + \ell \\
\text{H} & \\
\text{Et} & + \text{enantiomer and CH}_3 & + \ell \text{ Br} \\
\text{Et} & \\
\text{H} & + \text{CH}_3 & + \text{enantiomer}
\end{align*}
\]

ii) Br₂, H₂O

\[
\begin{align*}
\text{CH}_3 \text{CH}_2 & + \ell \text{ Br} \\
\text{CH}_3 \text{CH}_2 & + \ell \\
\text{OH} & \\
\text{Et} & + \text{enantiomer}
\end{align*}
\]

iii) H₂, Pt/C

\[
\begin{align*}
\text{CH}_3 \text{CH} & + \ell \\
\text{H} & + \text{CH}_3 & + \text{enantiomer}
\end{align*}
\]