Worksheet – Addition reactions

The presence of \( \pi \) electrons in alkenes allows \textbf{addition} reactions to take place. In general:

\[
\text{C} \equiv \text{C} \quad + \quad \text{Y} - \text{Z} \quad \rightarrow \quad \text{C} - \text{C} \quad \text{Y} \quad \text{Z}
\]

In each case, the \( \pi \) bond is broken and the \( e^- \) are used to form a new \( \sigma \) bond in the product molecule. We will look at the reaction mechanism for each of these processes, hydrohalogenation, hydration, halogenation and hydration. The \( \pi \) electrons are called a \textbf{nucleophile}, they are reactive \( e^- \) that can be used to form a new bond with a nucleus. They will react with \textbf{electrophiles}, species that are \( e^- \) deficient.

1. \textbf{Hydrohalogenation}, addition of H-Cl, H-Br or H-I.

These are \textbf{strong acids}, which dissociate completely to form H\(^+\) and X\(^-\).

In \textit{step 1} of this mechanism, the \( \pi \) electrons (nucleophile) will react with H\(^+\), an electrophile. Draw a curved arrow to indicate the flow of \( e^- \).

There will be 2 intermediates

\[
\begin{align*}
\text{step 1} & \quad \text{H} \equiv \text{C} - \text{C} - \text{CH}_3 \\
& \quad \quad \text{H} \equiv \text{C} - \text{C} - \text{CH}_3 \quad \quad \quad \text{H} \equiv \text{C} - \text{C} - \text{CH}_3 \quad \quad \quad \text{H} \equiv \text{C} - \text{C} - \text{CH}_3
\end{align*}
\]

Decide which is the major and which is the minor intermediate. Indicate the formal charges on the intermediates. Determine the order of the carbocations. Label the nucleophiles and electrophiles in the reactants.

Complete the mechanism with curved arrows and products. Again, label the electrophiles and nucleophiles.
2. **Hydration**, addition of water. The mechanism is very similar. The nucleophile is the \( \pi \) electrons. But, since water is not a strong acid, the [H\(^+\)] is very low (1 x 10\(^{-7}\)M). An acid catalyst must be provided.

Draw step 1 of the acid catalyzed addition of water to *cis*-3-methyl-2-pentene. Use curved arrows, show the major and minor intermediates, label the nucleophiles and electrophiles and the order of the carbocations.

*step 1*

In step 2 the carbocations (electrophiles) need nucleophiles to react with. The lone pair of electrons in water serves this function. Draw and label step 2 and you did for step 1. An oxygen with a positive charge is called an oxonium ion.

*step 2*

A third step is needed to remove the formal positive charge from O and regenerate the catalyst, H\(^+\). An O-H bond breaks, leaving both e\(^-\) on the oxygen as a lone pair, and releasing an H\(^+\), the catalyst. Draw and label step 3.

*step 3*

Verify your major product using Markovnikov’s rule (C with most H gets H).
3. **Bromination**, addition of Br₂

This is a diagnostic test for alkenes. Bromine is a rust colored compound. The color disappears as it is added across the C=C. No catalyst is needed.

In *step 1* the π electrons polarize the Br-Br molecule, to form Br⁺⁻⁻Br⁻⁻⁻. The Br⁺ (an electrophile) forms a bond with both carbons in C=C, giving a cyclic intermediate called a bromonium ion. The bromine bond breaks forming a bromide ion Br⁻.

\[ \text{Br}^- \rightarrow \text{Br}^- \]

In the next step, the Br⁻ moves to the other side of the molecule and forms a C-Br bond with a lone pair of electrons. The other C-Br bond breaks, re-forming a lone pair on the Br.

Because only the *trans* isomer forms, this is called a **stereospecific** reaction.

Draw and name the product of the bromination of *cis*-3,4-dimethyl-2-pentene.

This reaction turns alkenes (one degree of unsaturation, into alkanes (fully saturated). This is also a *stereospecific* reaction, with both H adding at the same time and to the same side of the C=C bond. This reaction is catalyzed by metal flakes. The metal adsorbs the hydrogen gas to its surface and weakens the H-H bond.

![Diagram of hydrogenation process](image)

In this case, only the *cis* isomer is formed.

Draw and name the product of the hydrogenation of *trans*-3,4-dibromocyclopentene.

5. Alkenes also undergo a **polymerization** reaction, in a free radical mechanism. (Single headed arrows indicate a single e⁻ is transferred).

![Polymerization reaction](image)

where \( n \) is a very large number.

Which alkene polymerized to give the compound shown below? (Hint, look at two adjacent C and see which substituents were on the C=C)

![Polymer](image)
Additional Problems:

6. Draw and categorize the carbocation intermediates formed by the reaction of \( \text{H}^+ \) and
   a. \( \text{CH}_2=\text{CH}_2 \)
   b. \( \text{CH}_2=\text{C}\left(\text{CH}_3\right)\text{CH}=\text{CH}_2 \)
   c. \( \text{CH}_3=\text{CH}=\text{CH}=\text{CH} \text{CH}_3 \)

7. Which of the following would react most rapidly with HI? Why?

   \( \text{CH}_2=\text{CH}_2 \) or \( \text{CH}_3\text{CH}=\text{CH} \text{CH}_3 \)
8. Draw the products (label as major or minor) of the reaction between 2-methyl-2-butene and
   a. \( \text{H}_2\text{O} (\text{H}^+) \)
   b. \( \text{Br}_2 \)
   c. \( \text{HBr} \)
   d. \( \text{H}_2 (\text{Pt}) \)

9. Draw the cycloalkene that reacts with \( \text{Cl}_2 \) to give:

   a) ![Image of a compound with three chlorine atoms]
   b) ![Image of a compound with one chlorine atom]
   c) ![Image of a compound with one chlorine atom and one methyl group]
   d) ![Image of a compound with one chlorine atom and one methylene group]
10. Draw and name the alkenes that give the following major products when they react with HCl:

   a. 
   
   b. 

11. Draw the alkene(s) which react with water and an acid catalyst to give: (There may be more than one)

   a. 

   b. 

   c. 

   d. 