Introduction to Alkenes and Alkynes

In an alkane, all covalent bonds between carbon were $\sigma$ (σ bonds are defined as bonds where the electron density is symmetric about the internuclear axis).

In an alkene, however, only three $\sigma$ bonds are formed from the alkene carbon—the carbon thus adopts an $sp^2$ hybridization.

Ethene (common name ethylene) has a molecular formula of $CH_2CH_2$.
Each carbon is $sp^2$ hybridized with a $\sigma$ bond to two hydrogens and the other carbon.

Hybridized orbital allows stronger bonds due to more overlap.
Structure of Ethylene

In addition to the $\sigma$ framework of ethylene, each carbon has an atomic $p$ orbital not used in hybridization.

The two $p$ orbitals (each with one electron) overlap to form a $\pi$ bond. ($p$ bonds are not symmetric about the internuclear axis)

$\pi$ bonds are not as strong as $\sigma$ bonds. (in ethylene, the $\sigma$ bond is $\sim 90$ Kcal/mol and the $\pi$ bond is $\sim 66$ Kcal/mol)

Thus while $\sigma$ bonds are stable and very few reactions occur with C-C bonds, $\pi$ bonds are much more reactive and many reactions occur with C=C $\pi$ bonds.
Nomenclature of Alkenes

August Wilhelm Hofmann’s attempt for systematic hydrocarbon nomenclature (1866)

Attempted to use a systematic name by naming all possible structures with 4 carbons

<table>
<thead>
<tr>
<th>Quartane</th>
<th>a</th>
<th>alkane</th>
<th>C_4H_{10}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartyl</td>
<td></td>
<td></td>
<td>C_4H_{9}</td>
</tr>
<tr>
<td>Quartene</td>
<td>e</td>
<td>alkene</td>
<td>C_4H_{8}</td>
</tr>
<tr>
<td>Quartenyl</td>
<td></td>
<td></td>
<td>C_4H_{7}</td>
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<tr>
<td>Quartine</td>
<td>i</td>
<td>alkine → alkyne</td>
<td>C_4H_{6}</td>
</tr>
<tr>
<td>Quartinyl</td>
<td></td>
<td></td>
<td>C_4H_{5}</td>
</tr>
<tr>
<td>Quartone</td>
<td>o</td>
<td></td>
<td>C_4H_{4}</td>
</tr>
<tr>
<td>Quartonyl</td>
<td></td>
<td></td>
<td>C_4H_{3}</td>
</tr>
<tr>
<td>Quartune</td>
<td>u</td>
<td></td>
<td>C_4H_{2}</td>
</tr>
<tr>
<td>Quartunyl</td>
<td></td>
<td></td>
<td>C_4H_{1}</td>
</tr>
</tbody>
</table>

Wanted to use Quart from the Latin for 4 – this method was not embraced and BUT has remained

Used English order of vowels, however, to name the groups (a, e, i, o, u)

This naming is the reason why we still call functional groups alkanes (saturated), Alkenes (having one double bond, thus lost 2 hydrogens) or alkynes (a triple bond) (the –ine suffix was replaced with –yne for ease in pronunciation)
Nomenclature of Alkenes

Alkenes use the same IUPAC nomenclature rules seen for alkanes

Main difference is want to find the longest carbon chain that contains the double bond

The alkene is numbered to indicate the position of the alkene
(want lowest number possible for alkene position)

If multiple alkenes, find chain that contains all polyenes as root

Some alkenes have isomers
(use E or Z designation)

Some common names:

vinyl

allyl

Alcohols have higher priority than alkenes
Double Bond Prevents Rotation

When a $\pi$ bond rotates, the energy of the bond is lost when orbitals are orthogonal.

With a $\sigma$ bond, rotation changes the steric energy but all bonds are still intact.

With a $\pi$ bond, rotation breaks the bond.

There is not enough thermal energy to allow bond rotation to occur.

~3.4 Kcal/mol

~66 Kcal/mol
Lack of Rotation Results in Isomers

Since at room temperature a double bond is “locked” into one conformation, isomers may result when different substituents are placed on the double bond

- if two substituents are on the same side of the double bond called CIS

\[
\begin{align*}
\text{cis-2-butene} & \quad \text{H}_3\text{C} & \quad \text{CH}_3 \\
\text{H} & \quad \equiv & \quad \equiv \\
\text{H} & \quad \text{H} & \quad \text{H}
\end{align*}
\]

- if two substituents are on opposite sides of the double bond called TRANS

\[
\begin{align*}
\text{trans-2-butene} & \quad \text{H}_3\text{C} & \quad \equiv \\
\text{H} & \quad \equiv & \quad \text{H} \\
\text{H} & \quad \text{CH}_3 & \quad \text{H}
\end{align*}
\]
Cahn-Ingold-Prelog Naming

If there are more than two substituents on a double bond, cis and trans have no meaning

Three chemists adopted a new naming method that is universally used (called Cahn-Ingold-Prelog or C-I-P)

In this method the substituents are “ranked” by priority

To rank priority:
1) Consider the atomic number of the atom directly attached (higher the atomic number, higher the priority)
2) For isotopes, atomic mass breaks the tie in atomic number
3) If still tied, consider the atoms bonded to the tied atoms. Continue only until the tie is broken.
4) Multiple bonds attached to an atom are treated as multiple single bonds. An alkene carbon therefore would consider as two bonds to that carbon

Consider the starred atom in this compound
Atoms attached: C, C, H, D
Using Cahn-Ingold-Prelog in Assigning Alkenes

-substituents are prioritized

Consider each end of the alkene separately

-if the highest priorities are on the same side called Z

\[
\begin{align*}
\text{Z} & \quad \text{zusammen} \quad \text{“together”} \\
2 & \quad \text{H}_3\text{C} \quad \text{H} \quad 2 \\
1 & \quad \text{Br} \quad \text{CH}_3 \quad 1
\end{align*}
\]

Z-2-bromo-2-butene

-if the highest priorities are on the opposite side called E

\[
\begin{align*}
\text{E} & \quad \text{entgegen} \quad \text{“opposite”} \\
2 & \quad \text{H}_3\text{C} \quad \text{CH}_3 \quad 1 \\
1 & \quad \text{Br} \quad \text{H} \quad 2
\end{align*}
\]

E-2-bromo-2-butene
Stability of Alkenes

In order to compare stability of different alkene structures, the structure must be considered.

Let us reconsider structures of reactive intermediates

A carbocation has three bonds to other atoms and only 6 electrons in outer shell.

Methyl cations are very unstable and rarely observed, but when extra alkyl substituents are attached the carbocation becomes more stable.

The reason for this extra stability is due partly to the adjacent C-H bond.

This bond can donate electron density to the empty p orbital of carbocation (hyperconjugation).

With carbocations this electron donation will lower the energy of the structure.

Alkyl groups are often considered “electron donating” due to this effect and thus:

3° cations > 2° cations > 1° cations > methyl cations

Rarely observed.

Another type of orbital mixing
Stability of Alkenes

Radicals are also electron deficient species, and thus more alkyl substituents will also stabilize them 
(3° radical > 2° radical > 1° radical > methyl radical)

Anions, however, are electron rich species 
-more alkyl substituents would raise the energy of an anion 
(methyl anion > 1° anion > 2° anion > 3° anion)

Alkenes are merely similar to two carbon radicals on adjacent atoms

Substituted alkene is more stable
(R group means any alkyl substituent)

E alkenes are more stable than Z

As number of substituents increases the alkene is more stable
Alkenes in Rings

A small ring (less than 8 carbons) can only have cis alkenes

![Cyclohexene](image)

It is sterically too high in energy to place a trans alkene in a ring smaller than 8 atoms (try building one with molecular models!)

A similar strain energy is present when trying to place an alkene in a bridgehead position

![Bridgehead carbon](image)  ![Not allowed](image)

bridgehead carbon  Not allowed

Called Bredt’s rule
(need at least 8 carbons in ring to allow an alkene in a bridgehead position)
Structure of Alkynes

Consider Acetylene
(common name for ethyne, the smallest possible alkyne)

The $\sigma$ bond is formed by combining an sp hybridized orbital on each carbon

The second sp hybridized orbital is used to form $\sigma$ bond to hydrogen

Each carbon has 2 atomic $p$ orbitals remaining which align to form two $\pi$ bonds

As the number of bonds increases between two carbons, the bond length decreases

- C-C triple bond bond length 1.20 Å
- C-C double bond bond length 1.33 Å
- C-C single bond bond length 1.54 Å
Alkynes

Many aspects of alkynes are similar to alkenes:

- A more substituted alkyne is more stable
  (there are only 2 possible substitution points for an alkyne though)

- Nomenclature for alkyne follows same rules
  (use –yne suffix instead of –ene)

  \[
  \text{(E)-3-methyl-3-decen-7-yne}
  \]

- Similar to trans alkenes, alkynes are not stable in a ring unless it is at least 8 carbons

- Small substituted fragments often have common names

  \[
  \begin{align*}
  \text{propargyl} & \quad \text{X} \\
  \text{allyl} & \quad \text{X}
  \end{align*}
  \]
Acidity of Alkynes

One effect of the increase in number of bonds (and bond length changes) is the acidity of an sp hybridized carbon-hydrogen bond.

As the resultant lone pair of electrons (the pair formed after the proton is abstracted in an acid-base reaction) becomes closer to the positively charged nucleus, the lone pair is MORE STABLE.

As the stability of the deprotonated form increases, the conjugate is more acidic.

Therefore, while abstracting an sp³ or sp² hybridized C-H is difficult, an sp hybridized C-H bond can easily be abstracted with common bases.
Acidity of Alkynes

Learn the acidity of terminal alkynes versus other alkyl groups and bases

\[
\begin{align*}
\text{CH}_3\text{CH}_3 & \quad \xrightarrow{\text{B}} \quad \text{CH}_3\text{CH}_2^- & \quad \text{pK}_a \approx 50-60 \\
\text{H} & \quad \xrightarrow{\text{B}} \quad \text{H}^- & \quad 44 \\
\text{NH}_3 & \quad \xrightarrow{\text{B}} \quad \text{NH}_2^- & \quad 35 \\
\text{H} & \quad \xrightarrow{\text{B}} \quad \text{H}^- & \quad 25 \\
\text{ROH} & \quad \xrightarrow{\text{B}} \quad \text{RO}^- & \quad 16
\end{align*}
\]

Therefore while alkoxides cannot deprotonate an alkyne, amides can easily deprotonate
Degrees of Unsaturation (Ω)

As we learned with saturated alkanes the molecular formula is \( C_n H_{2n+2} \)

With a monoalkene, however, the molecular formula is \( C_n H_{2n} \) and with alkynes it is \( C_n H_{2n-2} \)

\( \pi \) bonds are considered as a degree of unsaturation (each \( \pi \) bond results in 2 less hydrogens being attached to the molecule, thus unsaturation)

A cycloalkane is also a degree of unsaturation (to form a ring from a straight chain alkane, two hydrogens are removed and the two radical sites combine to form the ring)

The degrees of unsaturation (Ω) for a compound is thus stating the combined total of number of \( \pi \) bonds and the number of rings in a compound

If a molecular formula is given for a hydrocarbon, multiple the number of carbons by \( 2n+2 \), subtract the number of hydrogens in the actual compound from this number and then divide the difference by 2 (because each unsaturation removes 2 hydrogens) to determine Ω

If \( C_8 H_{14} \): 1) \( 8 \times 2n+2 = 18 \), 2) \( 18-14=4 \), 3) \( 4/2 = 2 \)
- Thus 2 degrees of unsaturation (compound has a combination of 2 \( \pi \) bonds and/or rings)
Introduction to Reaction of Alkenes and Alkynes

Alkenes generally react in an addition mechanism
(addition – two new species add to a molecule and none leave)

If hydrogen halides react, then a H and Cl add to the two ends of the double bond

\[
\begin{array}{c}
\text{H}_3\text{C} - \text{C} = \text{CH}_3 \\
\text{H} - \text{Cl} \rightarrow \text{H}_3\text{C} - \text{C} - \text{H}_3
\end{array}
\]

Since H-Cl is polarized, the H will be partially positively charged and Cl partially negative.

The alkene is thus the nucleophile and the proton is the electrophile.

As we first learned with acid/base reactions with Lewis definition, any reaction can be considered as a nucleophile reacting with an electrophile.

\[
\begin{array}{c}
\text{HOMO} \\
\text{reaction} \\
\text{LUMO}
\end{array}
\]

\{ \text{Energy gain} \}

nucleophile

product
Introduction to Reaction of Alkenes and Alkynes

When discussing mixing orbitals to form new orbitals there are two main considerations:

1) Amount of overlap between the orbitals that are mixing
2) How close in energy the two original orbitals are before mixing

Orbitals that overlap strongly and are close in energy will form two new molecular orbitals, one higher in energy and one lower in energy

When considering how a compound will react, and how readily it will react, the energy level of the HOMO and LUMO orbitals need to be determined

If the HOMO is high in energy, the compound will react as a nucleophile
(or base in acid/base terminology)

If the LUMO is low in energy, the compound will react as an electrophile
(or acid in acid/base terminology)

In every reaction we will study, it is important to recognize what is the nucleophile and what is the electrophile (or whether the compound has a high energy HOMO or a low energy LUMO)

But the question always becomes, “Compared to What?”
What is a high energy HOMO and what is a low energy LUMO?
Introduction to Reaction of Alkenes and Alkynes

As organic chemists we often compare bonds to something that is known to be unreactive, a carbon-carbon single bond.

C-C single bonds are relatively unreactive due to large overlap of sp\(^3\) hybridized orbital and energy match, therefore very low HOMO and high LUMO energy.

Atomic p orbital is higher in energy than sp\(^3\) (less s character) and the overlap for p orbitals is much less to form π bond.

Therefore orbitals do not mix as well for π bond and thus HOMO does not lower in energy nor LUMO raise in energy as much as σ bond (already had seen this with weaker π bond).

C-C π bond will thus be far more reactive, and it will react preferentially as the nucleophile due to higher HOMO level.
Introduction to Reaction of Alkenes and Alkynes

The reaction is thus a two step reaction  
The first step will generate a carbocation as a reactive intermediate 

\[
\text{H}_3\text{C} = \text{CH}_3 + \text{H}^+ \rightarrow \text{H}_3\text{C} - \text{CH}_2^+ \rightarrow \text{H}_3\text{C} - \text{CH}_2\text{H}_3 + \text{Cl}^-
\]

And the second step will have the carbocation react with the chloride to yield the product  
(the chloride is the nucleophile and the carbocation is the electrophile)

A reaction mechanism is often represented by a “reaction coordinate” diagram which graphs the energy of the species formed as the reaction progresses
The reaction coordinate indicates all structures formed in the reaction in a proper sequence.
Equilibrium Constants

Equilibrium constants ($K_{eq}$) indicate thermodynamically whether the reaction is favored in the forward or reverse direction and the magnitude of this preference.

\[ K_{eq} = \frac{[C][D]}{[A][B]} = \frac{\text{[products]}}{\text{[starting material]}} \]

\[ \Delta G \]

Reaction Coordinate

Potential energy
A second important feature is the RATE of a reaction

The rate is not determined by $K_{eq}$, But instead by the energy of activation $(E_a)$

Knowing the $E_a$ of a reaction tells us how fast a reaction will occur
Transition States vs. Intermediates

A transition state is an unstable species (it has no measurable lifetime)

An intermediate has a measurable lifetime (it can be isolated in theory)

The energy of activation refers to the energy difference between the starting material and the transition state along the reaction coordinate.
In a multistep reaction, the overall reaction rate is determined by the highest energy barrier along the reaction coordinate.

Referred to as the rate determining step:

\[ E_a(1) > E_a(2) \]
Regiochemistry of Alkene Additions

When E-2-butene was reacted with HCl, only one product can be obtained

\[
\text{H}_3\text{C} = \text{CH}_2 + \text{HCl} \rightarrow \text{H}_3\text{C} - \text{CH}_2\text{Cl}
\]

When an unsymmetrical alkene like propene is reacted, however, two possible products are obtained (2-chloropropane or 1-chloropropane) (resulting from H and Cl adding to different ends of alkene)

Since the carbocation is the high energy structure along the reaction coordinate, the energy of activation will be determined by the stability of the possible carbocations in the first step

Since 2° carbocations are more stable than 1°, 2-chloropropane is the only product obtained
Hydration Reactions with Alkenes

When a weaker electrophile is being used, a catalyst is needed for alkene reactions to occur.

An example is reaction with water.

Water will not react with alkenes directly, but with proper catalyst it will react.

Will still follow same regiochemistry as seen with HCl addition.

Many other reactions will be observed in later chapters, but all reactions follow these similar rules – nucleophiles react with electrophiles. If you can determine the nucleophile and electrophile in a reaction the products are straightforward.