

Ch 7 Alkenes – Structure and Reactivity

- Alkenes (or olefins) contain a double bond, and are often prepared industrially by thermally “cracking” small alkanes at $\sim 900\text{ }^\circ\text{C}$.
- Cracking has a high endothermic ΔH° because strong σ bonds are broken.
- But ΔS° is also positive because molecules are split into pieces (increases disorder).
- The result is a negative ΔG° at high T, where the reaction becomes spontaneous.

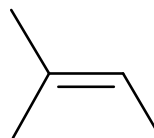
Degree of Unsaturation

- This is the total combined number of Π bonds and rings in a molecule.
- For C_nH_x , the degree is $\left(\frac{1}{2}\right)[(2n+2) - (x)]$
- For substituted molecules, add the number of halogens to the number of H's, and subtract the number of N's from the number of H's. Ignore the number of O's completely.
- So, the result is $\left(\frac{1}{2}\right)[(2n+2) - (x + \text{halogens} - \text{N's})]$
- For instance, if we have the condensed formula $\text{CH}_2\text{CHCONCl}_2$, then $n = 3$, $x = 3$, halogens = 2, and $N = 1$.
So, the degree of unsaturation = $(1/2)[(8) - (3 + 2 - 1)] = ?$

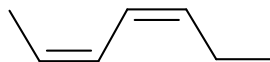
Nomenclature Rules

- 1) Parent is the longest chain that **contains** the double bonds.
- 2) Number the C's starting at the end **nearest** to the double bond.
If there is a choice, pick the end nearest to the first branch point.
- 3) Write the name by putting the C number's for the double bonds in front of the parent name.
(A newer system puts the double bond number's directly before the -ene or -diene.)
Use **diene** or **triene** if there is more than one double bond.

- This molecule is 2-methyl-2-butene (or 2-methylbut-2-ene):
Is it *cis* or *trans*?

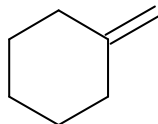


- This molecule is *cis,cis*-2,4-heptadiene:
Here, both double bonds are *cis*.

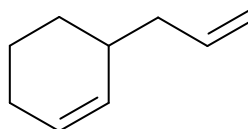


- There are also common names for some substituents with double bonds:
 $\text{H}_2\text{C}=\text{}$ is methylene, $\text{H}_2\text{C}=\text{CH}-$ is vinyl (ethenyl), and $\text{H}_2\text{C}=\text{CHCH}_2-$ is allyl.

- This molecule is methylenecyclohexane:



- For cycloalkenes, C's 1 and 2 will cross the double bond.
For instance, this molecule at right is 3-allylcyclohexene:



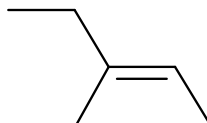
Electronic Structure

- π bonds need to break before σ bonds can rotate, which require a lot of energy.
- So, cis and trans are separate stereoisomers that do **not** easily interconvert.

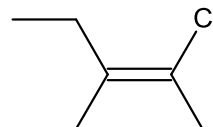
E and Z (the Cahn, Ingold, Prelog sequence rules)

- If a double bond has more than two substituents, then cis/trans does not really apply.
- The priority of both substituents on each C is determined.
- If the two high priority substituents are on the **same** side, then the molecule is **Z** (“Zee same side”).
- If they are on **opposite** sides, the molecule is **E** (“Epposite”).
- The rules are:
 1. Higher atomic number (**Z**) gets higher priority ($\text{Br} > \text{Cl} > \text{O}$).
 2. If both atoms are the same, look at the following atoms ($\text{BrO} > \text{HO}$).
 3. Count double and triple bonded substituents as an equivalent number of single bonds.

- This molecule is E-3-methyl-2-pentene:



- But, this molecule is Z-2-chloro-3-methyl-2-pentene:



Stability of Alkenes

- Cis and trans can interconvert with an acid catalyst.
- Trans predominates because it is more stable (has less steric strain).
- For 2-butene, $\text{cis} \rightleftharpoons \text{trans}$ results in 76% (by mole) in the mixture being trans at 25 °C,

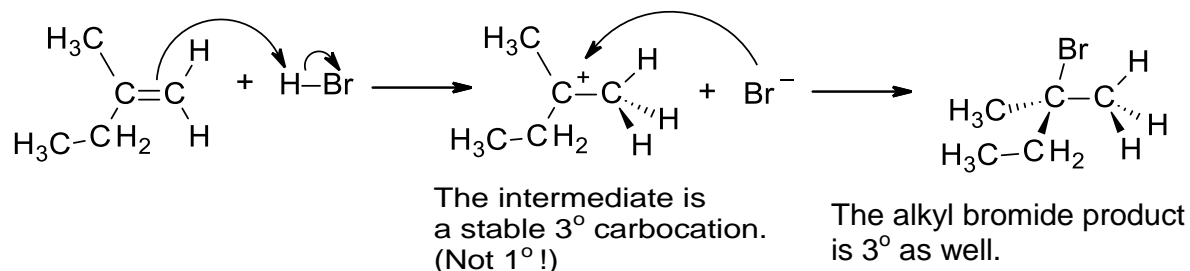
$$K = \frac{[\text{trans}]}{[\text{cis}]} = \frac{76}{24} = 3.17 \quad \Delta G^\circ = - (RT)\ln[K] = - 2.8 \text{ kJ/mol}$$

The forward reaction is spontaneous, and equilibrium favors the trans product.

- The combustion of cis-2-butene (less stable) is more exothermic than that of trans. Hydrogenation of cis is more exergonic than that of trans, as well.
- The more substituted alkene is more stable: tetra > tri > di > mono > C_2H_4 .
- The stability results partially from hyperconjugation, which is an interaction between the π^* molecular orbital and the neighboring C-H σ bond. These orbitals essentially create a lower energy molecular orbital that contains the σ bond e^{-1} 's.
- Stability also results because the $\text{sp}^2\text{-sp}^3$ single bond is shorter and stronger than the $\text{sp}^3\text{-sp}^3$ single bond. 2-butene's two C-C single bonds are both $\text{sp}^2\text{-sp}^3$ single bonds, while 1-butene has one (weaker) $\text{sp}^3\text{-sp}^3$ single bond and one $\text{sp}^2\text{-sp}^3$ single bond.

Electrophilic Addition of HX to C=C

- The 1st step has H⁺ as the E⁺, while the 2nd has the carbocation as the E⁺.
- Step 1 has a high E_a and produces a reactive carbocation, so it is **slow** and **endergonic**.
- Step 2 has a low E_a and creates a stable alkyl bromide, so it is **fast** and **exergonic**.



Markovnikov's Rule

- For addition of HX to an alkene, the H goes on the less substituted C, and X goes on the more substituted C.
- Therefore, the more **highly substituted** carbocation is formed as the intermediate.
- This is called regioselective.

Carbocation Stability

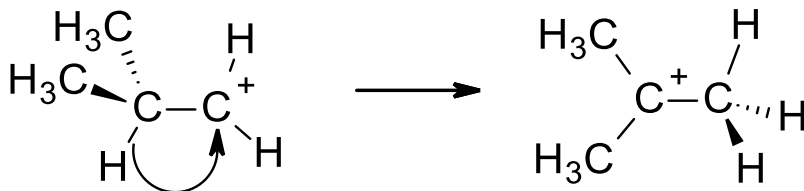
- The more highly substituted carbocation is more stable, due to hyperconjugation, as well as inductive effects.
- Induction essentially means σ bonds have been polarized, which happens if the bonds are either polar or polarizable.
- That is, the e⁻'s from polarizable alkyl groups can shift their e⁻ density towards the positive charge.
- So, a more substituted carbocation has more e⁻ density to stabilize the positive charge.
- The stability trend is 3° > 2° > 1° > methyl

The Hammond Postulate

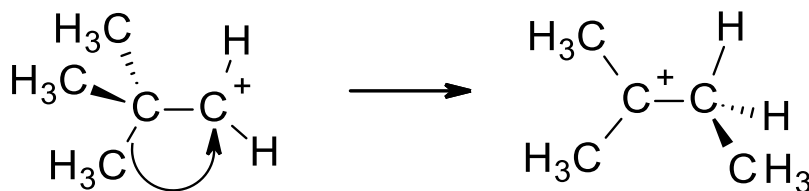
- The more highly substituted carbocation forms faster during electrophilic addition because it has a lower E_a, and it is favored overall because it has a lower overall energy and is more stable.
- The Hammond Postulate states that an endergonic reaction (1st step) has \ddagger structure closer to the product, and an exergonic reaction (2nd step) has \ddagger closer to the reactant.
- So, more stable carbocations are formed faster because \ddagger is also more stable (lower E_a), and both \ddagger and the carbocation are stable for the same reasons.

Carbocation Rearrangements

- They can rearrange (isomerize) to become more stable carbocations.
- **Hydride** shifts occur when H^- (along with the $2e^-$) moves to the C^+ to form a different, more-substituted carbocation.
- For example, in the hydride shift below, a 1° carbocation becomes 3° .



- **Alkyl** shifts occur when R^- (alkyl group with the $2e^-$) moves to the C^+ , also forming a different, more-substituted carbocation.
- For example, in the methyl shift below, a 1° carbocation becomes 3° .



- In either case, a more stable, more-substituted cation is formed.
- Essentially, a 1° cation will rearrange if possible to become 2° or 3° , and a 2° cation will rearrange if possible to become 3° .