

Week 6

Reactions of Alkenes

6.1 Alkene Nomenclature and Reactions

11/2:

- Alkene nomenclature.
- Degree of unsaturation, aka hydrogen deficiency.
 - Indicate the sum of the number of rings and π bonds in a molecule simply by examining the formula.
 - Recall for hydrogens and other heteroatoms (e.g., oxygen, nitrogen, halogens, etc.).
- Reactions of alkenes:
 - Important because an understanding of reactions enables us to do syntheses.
 - There are three components in a chemical reaction: The reactants, products, and conditions.
 - We should be able to predict any one of these from the other two.
 - We should also be able to draw the reaction mechanism.
- **Reaction mechanism:** A stepwise description of what happened in the reaction.
 - This involves arrow pushing.
- Know Table 6.1 from the textbook (carbon-halogen bond lengths and bond strengths).
- **Hydrohalogenation:** Addition of H-X across a C=C double bond.

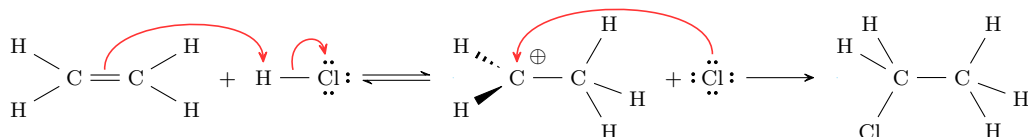


Figure 6.1: Hydrohalogenation mechanism.

- We add the H to one of the alkene carbons and the X to the other.
- Since H-X likes electrons, it is the **electrophile**.
- If a carbocation is formed, you have an **electrophilic addition reaction**.
- For unsymmetric alkenes, we add the X to the more substituted position since a carbocation will form there during the mechanism and be stabilized by **hyperconjugation**.
 - This is Markovnikov addition.

- **Hyperconjugation:** Adjacent C–H bonding electrons donate electron density into vacant p orbitals (of C^+), thus stabilizing the carbocation.

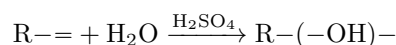
– Thus, alkyl groups are considered electron-donating groups because they delocalize positive charges through inductive effects.

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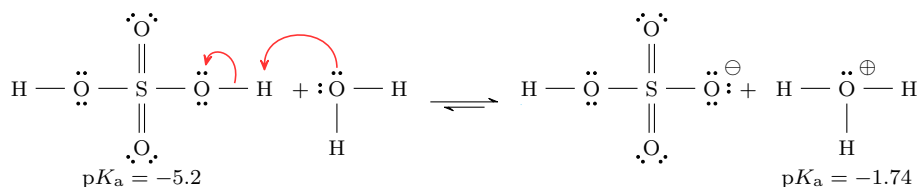
- **Markovnikov addition:** The side of the alkene with more H's gets the H.
- Energy diagram of hydrohalogenation.
 - Energy of the product is lower than the energy of the reactants (this is an exergonic reaction).
 - Energy of the intermediate is higher than either reactants or products.
 - The first transition state is higher energy than the second.
 - The first activation energy is significantly greater than the second (thus, the first step is slow).
 - Driving force: Thermodynamics — more stable product. This makes sense since we're breaking one π bond and one σ bond and forming two σ bonds, and σ bonds are stronger than π bonds.
- Introduces methyl/hydride 1,2-shifts to form a more stable, more substituted carbocations.
 - Is there enough of a driving force to go from a primary to a secondary carbocation, or a secondary to a tertiary carbocation, or is it just a primary to a tertiary carbocation?

- Acid-catalyzed hydration.

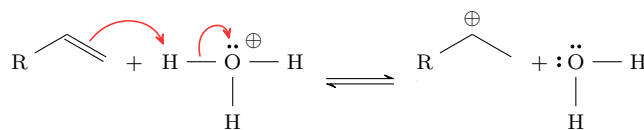
- General form:



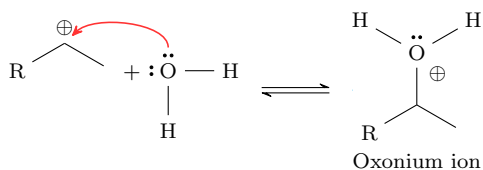
- Mechanism:



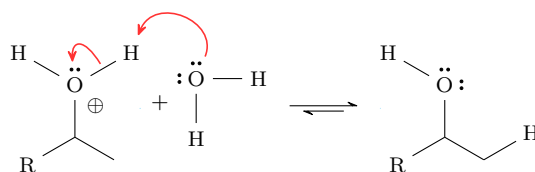
(a) Acid dissociation.



(b) First step.



(c) Second step.



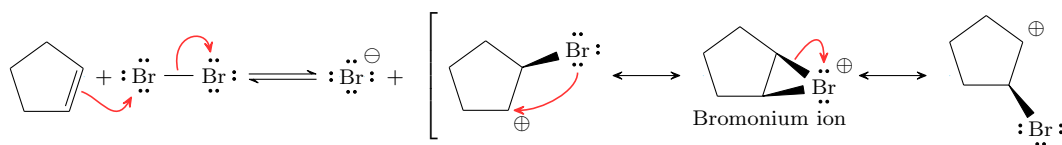
(d) Third step.

Figure 6.2: Acid-catalyzed hydration mechanism.

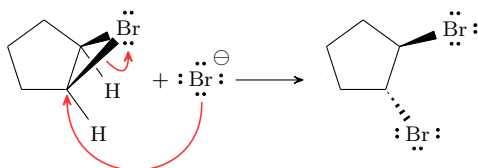
- Thus, the hydronium ion is a catalyst.
- Same regioselectivity — this is Markovnikov addition.
- Same possibility for 1,2-shifts.
- Racemic mixture of product since the carbocation is sp^2 planar and water has equal probability of attacking both faces.
- Replacing H_2O with ROH : Just replace OH in the product with OR.
 - This is a way to make ethers. More on this third quarter.
- Addition of X_2 to alkenes (typically Br_2 or Cl_2).
- General form:

$$\text{alkene} + \text{X}_2 \xrightarrow{\text{CCl}_4} \text{X}-\text{CH}_2-\text{CH}_2-\text{X}$$
 - Generates the *trans*-product only, if there is a choice.
 - Thus, the reaction does not proceed through a carbocation mechanism.
- Consider Br_2 first.
 - Each bromine is very electronegative.
 - Thus, the bond is weak since both atoms are fighting for electrons.
 - Think about Br_2 as Br^+Br^- .
 - Thus, Br_2 is a very good electrophile.

- Mechanism:



(a) First step.

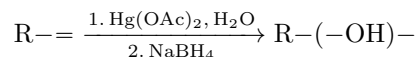


(b) Second step.

Figure 6.3: Halogenation mechanism.

- Note that in the first step, the bromonium ion will be the major contributing structure because it satisfies the octet rule and it's symmetrical. This is why we show only it in the second step.

- In the second step, because of the steric hindrance of the bromonium ion, the bromide ion engages in a “special attack” from the back side, resulting in the *trans* geometry. Note that it can attack either carbon, not just the one shown in Figure 6.3b.
- When we use chlorine, the reaction proceeds through a chloronium ion.
- Trapping the bromonium or chloronium ion.
 - These ions can be trapped by H₂O, leading to a bromo/chloro-alcohol.
 - This reaction is both regiospecific and stereospecific.
 - It proceeds through a mechanism that is the natural cross between the halogenation and acid-catalyzed hydration mechanism.
- Take-home message: The more substituted carbon has more cationic character, so it tends to be attacked more by the nucleophile.
- Oxymercuration.
- General form:



- NaBH₄ is a very good hydrogen source (more on this second and third quarter).
- The mechanism proceeds through a mercurinium ion that is trapped by water, and the resulting mercury acetate ligand is replaced with a hydride ligand by NaBH₄.
- No possibility for hydride/methyl shifts.