Chemistry 343

Lecture 19

Topics

Electrophilic Addition Reactions of Alkenes
  HX addition
  H₂O addition
  X₂ addition

The halohydrin reaction

Electrophilic Addition Reactions of Alkynes

Oxidation of Alkenes

Oxidation of Alkynes

Props/Demos

Large model of 2-butene
II. Electrophilic Addition Reactions

A. Alkenes as nucleophiles

The end of double bonds are relatively far from carbon nuclei, accessible and polarizable. This makes them very susceptible to attack by electrophiles.

B. H-\text{X} Addition Reactions

\[
\text{CH}_3\text{CH}=\text{CHCH}_3 + \text{HBr} \rightarrow \text{CH}_3\text{CH}_2\text{C} - \text{CH}_3^+ \rightarrow \left[ \text{CH}_3\text{-CH}_2\text{-CHCH}_3 \right] \rightarrow \text{Regiochemistry}
\]

2. With unsymmetrical alkenes

\(\text{H}^+\) adds to less substituted carbon forming more stable carbocation.

\[
\text{CH}_3\text{CH} = \text{CH}_2 + \text{HBr} \rightarrow \text{CH}_3\text{-C} - \text{Br} \rightarrow \left( \text{CH}_3 \right)_2\text{C} - \text{Br} \text{ major product}
\]
3. Markovnikov's Rule - In addition of H-X to alkenes, H\(^+\) adds to the less substituted carbon and X\(^-\) adds to the more substituted carbon.

Alternatively stated: H-X addition reactions proceed via most stable carbocation.

To remember Zaitsev and Markovnikov rules: The rich get richer and the poor get poorer.

4. So H-X additions to alkenes are regioselective.

5. Stereochemistry.

In many cases, such as addition of HBr to 2-Butene shown above, H-X addition to an alkene creates a stereo center, but in all such cases, the product is a racemic mixture.
C. Hydration Reactions

1. Just the reverse of dehydration reactions of alcohols.

\[ \text{CH}_3 - \text{CH} = \text{CH}_2 \xrightarrow{\text{H}^+ / \text{H}_2\text{O}} \text{CH}_3 - \text{CH} - \text{CH}_3 \]

(\text{key difference is dilute acid solution for addition reaction})

\[ +\text{H}^+ \rightarrow \text{CH}_3 - \text{CH} = \text{CH}_2 \xrightarrow{\text{H}^+ / \text{H}_2\text{O}} \text{CH}_3 - \text{CH} - \text{CH}_3 \]

Hydration follows Markovnikov Rule.