Electrophilic and free radicals' addition

Reactions at Carbon–Carbon Double Bond

Understanding the Double Bond (C=C)

- The carbon–carbon double bond in alkenes consists of one sigma (σ) bond and one pi (π) bond.
- The sigma bond is formed by head-on overlap of sp^2 hybrid orbitals, while the pi bond is formed by the lateral overlap of unhybridized p orbitals.
    - The pi bond is less strong and more exposed compared to the sigma bond, making it the primary site of reactivity in electrophilic and free radical additions.
    - The electron density above and below the plane of the molecule due to the pi bond makes it electron-rich, which allows electrophiles (electron-deficient species) to attack.

Electrophilic Addition Mechanism

- This is the most common reaction mechanism for alkenes, especially under acidic conditions or with polar reagents.

General mechanism:

1. **Attack by Electrophile (E^+):**
    - The pi electrons of the double bond attack the electrophile.
    - A carbocation intermediate is formed.
    - Example: In the presence of HBr, the alkene uses its π electrons to attack H^+ from HBr, forming a carbocation and Br^-.
2. **Nucleophilic Attack:**
    - The nucleophile (like Br^-) attacks the carbocation to complete the reaction.
    - **Example:**

$$CH_2 = CH_2 + HBr \rightarrow CH_3CH_2Br$$

3. This mechanism can involve **rearrangements** if more stable carbocations can be formed.

Mechanism of Free Radical Addition of HBr (Peroxide Effect):

1. **Initiation:**
    - ROOR (peroxide) decomposes into two alkoxy radicals under heat/light:

$$ROOR \rightarrow 2RO\cdot$$

2. **Propagation:**
    - Alkoxy radical abstracts a hydrogen atom from HBr:

$$RO\cdot + HBr \rightarrow ROH + Br\cdot$$

    - The Br radical adds to the double bond, forming a carbon radical:

$$CH_2 = CH_2 + Br \cdot \rightarrow CH_2CH_2 \cdot$$

- The carbon radical abstracts H from another HBr:

$$CH_2CH_2 \cdot + HBr \rightarrow CH_3CH_2Br + Br \cdot$$

3. Termination:

- Two radicals recombine, ending the chain:

$$Br \cdot + Br \cdot \rightarrow Br_2$$

Notably, this reaction only works with HBr, not HCl or HI due to bond energy differences and radical stability.

Comparison Between Electrophilic and Free Radical Additions

Feature	Electrophilic Addition	Free Radical Addition
Reagents	HX (no peroxide), X_2, etc.	HBr + peroxide
Mechanism	Carbocation intermediate	Radical intermediate
Orientation	Markovnikov	Anti-Markovnikov
Conditions	Room temperature, acid catalyst	Peroxide, light/heat
Commonality	Very common	Less common, selective

Electrophile

Definition and Basic Concept

- An electrophile is a species that is electron-deficient and seeks electrons.
- It is the chemical counterpart of a nucleophile, which donates electrons.
  - Etymology: From Greek "electron" (amber, electricity) and "philos" (loving) — "electron-loving".
  - Electrophiles are Lewis acids because they accept electron pairs.

Types of Electrophiles

1. Neutral Electrophiles:

- Molecules with partial positive centers due to polarization.
- Examples:
  - H_2SO_4 (sulfur is electron-deficient)
  - SO_3
  - Br_2 and Cl_2 (polarizable molecules)

2. Positively Charged Electrophiles:

- Cations with a positive charge.
- Examples:
  - H^+, NO_2^+, R^+ (carbocations), Fe^{3+}, $AlCl_3$ (acts as Lewis acid)

Electrophilicity and Reactivity

- Electrophilicity depends on:
  - **Charge**: Higher positive charge increases electrophilicity.
  - **Size**: Smaller electrophiles are more reactive.
  - **Polarizability**: The ease with which the electron cloud can be distorted (e.g., Br_2, Cl_2).
  - **Solvent Effects**: Polar solvents can stabilize charged species and influence reactivity.

Electrophiles in Addition Reactions

- In alkene chemistry, electrophiles attack the pi bond due to its electron-rich character.
- This makes alkenes excellent substrates for reactions with electrophiles.
- **Example:**

$$\mathbf{CH_2 = CH_2 + HBr \rightarrow [CH_3CH_2]^+ + Br^- \rightarrow CH_3CH_2Br}$$

  - The **carbocation** formed is also an electrophile and can further undergo rearrangement.
  - Electrophiles are central in:
  - Electrophilic addition
  - Electrophilic aromatic substitution
  - Electrophilic substitution of enolates/enamines

Hydrogenation of Alkenes

Definition

- Hydrogenation is the addition of hydrogen (H_2) across a carbon–carbon double bond to form a saturated alkane.
- It is an example of a syn-addition, as both hydrogen atoms are added to the same face of the double bond.

Catalysts Used

- This reaction does not occur without a catalyst.
- Common catalysts include:
  - **Heterogeneous Catalysts**: Ni, Pd, Pt on a solid surface
  - **Homogeneous Catalysts**: Wilkinson's catalyst [$(Ph_3P)_3RhCl$]

Mechanism (Heterogeneous)

1. Adsorption of hydrogen gas on the metal catalyst surface.
2. Adsorption of the alkene on the same surface.
3. Migration of H atoms to the alkene – both H atoms add to the same face (syn).
4. Desorption of the newly formed alkane from the surface.

- **Example:**

$$CH_2 = CH_2 + H_2 \xrightarrow{Ni} CH_3CH_3$$

Selectivity and Stereochemistry

- **Syn-addition**: Both hydrogen atoms add on the same side.
- **Stereoselectivity**: Important in cyclic alkenes and for chiral centers.
- **Regioselectivity**: Not applicable as both H atoms are the same.

Thermodynamics

- Hydrogenation is exothermic:
  - It releases energy (negative ΔH).
  - The magnitude of this heat is known as the heat of hydrogenation, which gives insights into the stability of the alkene.

Applications

- Synthesis of margarine from unsaturated vegetable oils.
- Petrochemical industry for converting alkenes to alkanes.

Heat of Hydrogenation and Stability of Alkenes

Heat of Hydrogenation (ΔH_hydrogenation)

- Heat of hydrogenation refers to the amount of heat released when one mole of an alkene undergoes hydrogenation (addition of H_2) in the presence of a metal catalyst to form an alkane.
  - It is a negative value because hydrogenation is an exothermic process.
  - Units are usually kJ/mol or kcal/mol.
  - The greater the amount of heat released, the less stable the alkene.

Measuring Stability Using Heat of Hydrogenation

- The thermodynamic stability of an alkene can be inferred by comparing its heat of hydrogenation.
- Alkenes with lower heats of hydrogenation are more stable.

Stability trend (based on substitution)

- Tetrasubstituted < Trisubstituted < Disubstituted < Monosubstituted < Ethylene

  (most stable) (least stable)

- Each additional alkyl group stabilizes the double bond via hyperconjugation and inductive effects, reducing the energy released on hydrogenation.

Factors Affecting Alkene Stability

1. Substitution Pattern:

- More alkyl groups on the double bond → more stability.
- Follows the order: Tetra > Tri > Di (trans > cis) > Mono.

2. Conjugation:

- Alkenes conjugated with π systems (e.g., dienes, aromatic rings) are more stable.

3. Ring Strain:

- Cycloalkenes show decreased stability due to angle strain (notably in small rings).

4. Steric Effects:

- Bulky groups near the double bond can destabilize the molecule, especially in cis-isomers.

5. Resonance:

- Alkenes involved in resonance with adjacent lone pairs or π bonds are more stable.

Comparison of Stability Based on Heat of Hydrogenation:

Alkene Type	Example	Heat of Hydrogenation (approx.)	Stability
Mono-substituted	CH_2=$CHCH_3$	~30 kcal/mol	Least stable
Di-substituted (cis)	cis-2-butene	~27.6 kcal/mol	Less stable than trans
Di-substituted (trans)	trans-2-butene	~26.9 kcal/mol	More stable
Tri-substituted	2-methyl-2-butene	~26 kcal/mol	Even more stable
Tetra-substituted	2,3-dimethyl-2-butene	~25 kcal/mol	Most stable

- This trend demonstrates that more substituted alkenes are more stable due to:
  - Hyperconjugation
  - Alkyl group electron-donating effects
  - Less steric strain in trans isomers

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