Nucleophilic Addition Reaction

Nucleophilic Addition Reaction: Mechanism

Definition:

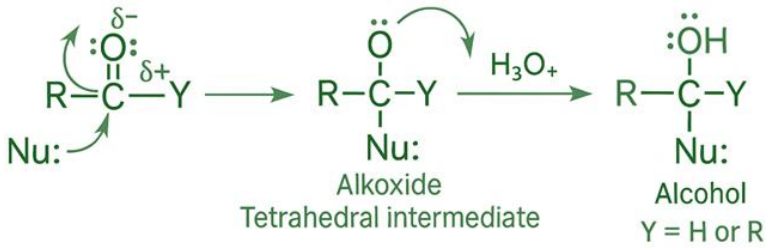
- A nucleophilic addition reaction is a type of chemical reaction in which a nucleophile adds to an electron-deficient carbon atom, typically the carbon of a carbonyl group (C=O).
- These reactions are most common in aldehydes and ketones because they contain a polar carbonyl group.

Why It Happens:

- The carbonyl carbon is electrophilic due to the difference in electronegativity between carbon and oxygen.
- Oxygen pulls the electron density towards itself, making the carbon partially positive (δ+).
- A nucleophile, which is rich in electron density (like OH^-, CN^-, R^-, or even water), is attracted to this partial positive center.

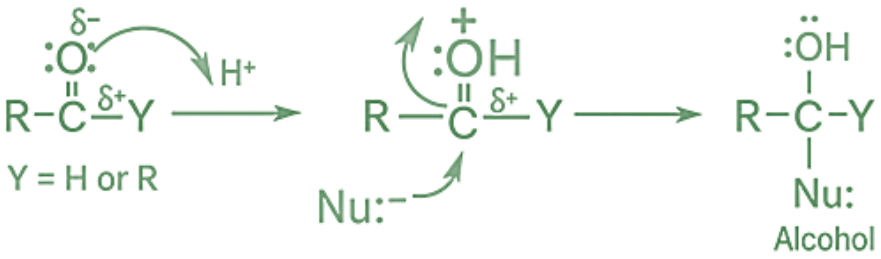
Step-by-Step Mechanism

1. **Nucleophilic Attack on the Carbonyl Carbon**
   - A nucleophile (electron-rich species) attacks the electrophilic carbonyl carbon.
   - This breaks the π bond of the carbonyl, forming a tetrahedral alkoxide intermediate.



$R_2C{=}O + Nu^- \rightarrow R_2C(^-O^-)(Nu)$

2. **Protonation of the Alkoxide Intermediate**
   - The intermediate alkoxide ion is protonated by a proton donor (e.g., water, acid).
   - This gives the final addition product, typically an alcohol.



$R_2C(^-O^-)(Nu) + H^+ \rightarrow R_2C(OH)(Nu)$

Role of Acid and Catalysis

Strong vs. Weak Nucleophiles

- **Strong nucleophiles** (e.g., OH^-, RO^-, H^-): React without need for activation.

- **Weak nucleophiles** (e.g., H_2O, ROH): Need **acid catalysis** to proceed efficiently.

Acid Catalysis Mechanism

1. **Protonation of the Carbonyl Oxygen:**
   - Acid (H^+) protonates the oxygen atom of the carbonyl group.
   - This increases the **positive charge on the carbon**, making it **more electrophilic**.

$$R_2C{=}O + H^+ \rightarrow R_2C{=}OH^+$$

2. **Attack by Weak Nucleophile:**
   - Now the nucleophile (like water or alcohol) can attack more easily.
   - Followed again by deprotonation to stabilize the product.

Example: Addition of HCN to Aldehyde

Aldehyde (RCHO) + HCN → Cyanohydrin (RCH(OH)CN)

1. CN^- attacks carbonyl carbon.
2. Intermediate alkoxide forms.
3. Alkoxide gets protonated → OH group.

Ionisation of Carboxylic Acids

Overview:

- Carboxylic acids contain the –COOH group, which can lose a proton (H^+) to form a carboxylate anion ($–COO^-$). This process is called ionisation.

Ionisation Equation:

$$R–COOH \rightleftharpoons R–COO^- + H^+$$

Factors Involved:

1. **Nature of the –COOH group:**
   - The carboxyl group has resonance stabilization between the two oxygen atoms in the carboxylate ion, which promotes ionisation.
2. **Solvent (usually water):**
   - Water stabilizes the ions formed by solvation (hydration), especially the H^+ ion.
3. **Resonance:**
   - The carboxylate ion formed ($RCOO^-$) is **resonance-stabilized**.
   - The negative charge is delocalized equally over both oxygen atoms, making it more stable than the undissociated acid.

$$O{=}C–O^- \rightleftharpoons {}^-O–C{=}O$$

4. **Electronegativity:**

- The electronegative oxygen atoms attract electron density, making the proton more acidic.

Why carboxylic acids ionise:

- After deprotonation, the resulting carboxylate ion is resonance stabilized:
- This delocalisation of negative charge over two oxygen atoms stabilises the anion, making the loss of a proton favorable.

Influencing Factors:

- **Solvent**: Polar solvents like water stabilize ions and promote ionisation.
- **Temperature**: Higher temperatures can shift the equilibrium.

Acidity Constants (Ka and pKa)

What is Ka?

- Ka is the acid dissociation constant, a measure of the extent of ionisation of an acid in water.
- It is defined by the equilibrium expression:

$$Ka = [R–COO^-][H^+] / [R–COOH]$$

What is pKa?

- pKa is the negative logarithm of Ka:

$$pKa = –\log Ka$$

- A lower pKa means a stronger acid.

Acidity Constant (Ka):

- The acid dissociation constant, Ka, quantifies the extent of ionisation of a weak acid in solution.
- Higher Ka → stronger acid (greater tendency to donate H^+).
- It is defined for the equilibrium:

$$HA \rightleftharpoons H^+ + A^-$$

$$Ka = \frac{[H^+][A^-]}{[HA]}$$

Where:

- [HA] = concentration of undissociated acid
- $[H^+]$ = hydrogen ion concentration
- $[A^-]$ = concentration of conjugate base (anion)

Importance in Carboxylic Acids:

- The carboxyl group (–COOH) is more acidic than alcohols due to the resonance stabilization of the carboxylate ion.

- Typical pKa values of simple carboxylic acids range between 4–5.

Factors Influencing Ka/pKa:

A. Inductive Effect:

- Electron-withdrawing groups (like –Cl, $–NO_2$) near the –COOH group increase acidity by stabilizing the carboxylate ion, leading to higher Ka (lower pKa).

B. Resonance:

- Greater resonance delocalization in the carboxylate ion increases stability, hence stronger acidity.

C. Hybridization of the Carbon:

- The sp^2 hybridized carbon of the –COOH group increases acidity relative to other functional groups with sp^3 carbons (like alcohols).

D. Solvent Effect:

- Protic solvents stabilize ions better and increase Ka.

Acidity of Acids

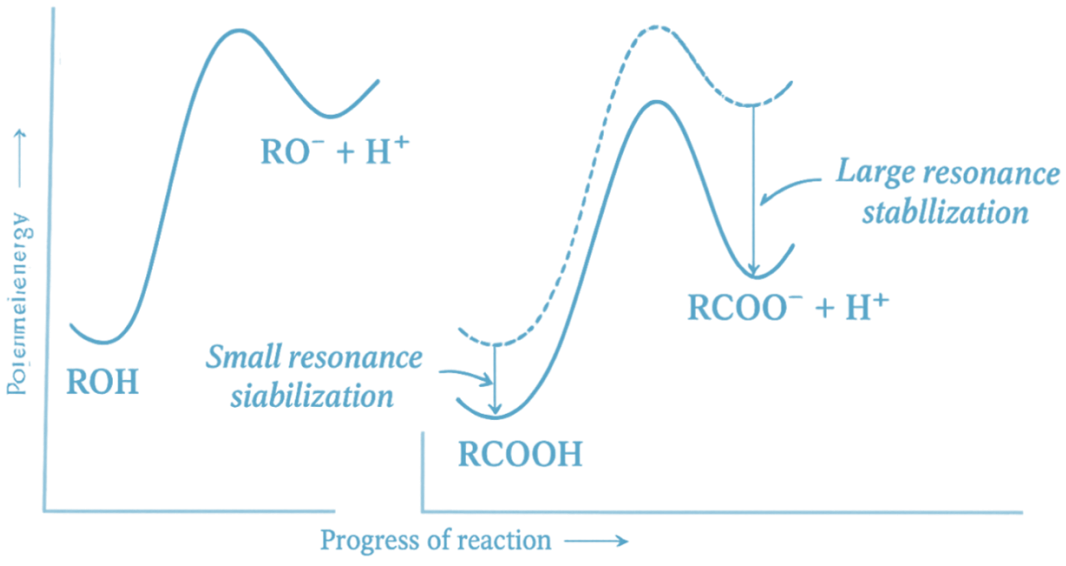
Overview

- The acidity of a compound refers to its ability to donate a proton (H^+).
- For carboxylic acids, this acidity is influenced by the structure of the acid and various electronic factors.

Why are carboxylic acids acidic?

- Carboxylic acids contain the –COOH group.
- When the hydrogen ion (proton) is removed from the hydroxyl (–OH) part of the carboxyl group, a carboxylate ion ($–COO^-$) is formed.
- The stability of this ion is a key reason for the acidity of carboxylic acids.

$$R–COOH \rightleftharpoons R–COO^- + H^+$$



Key Factors That Influence Acidity:

1. **Resonance Stabilization:**
   - The negative charge on the carboxylate ion is delocalized between the two oxygen atoms.
   - Resonance makes the ion more stable, making proton loss (acid behavior) easier.
2. **Inductive Effect:**
   - Electron-withdrawing groups (like Cl, NO_2) near the –COOH group pull electron density away, stabilizing the negative charge on the carboxylate ion.
   - This increases acidity.
   - Conversely, electron-donating groups (like CH_3) push electrons toward the $–COO^-$ group, destabilizing the ion and decreasing acidity.
3. **Hybridization:**
   - Acidity increases with increasing s-character of the atom bonded to hydrogen.
   - But in carboxylic acids, hybridization has less influence compared to resonance and inductive effects.
4. **Hydrogen Bonding & Solvent Effects:**
   - In polar solvents like water, ionization is favored due to solvation (hydration) of ions.
   - Intramolecular hydrogen bonding can also influence acidity.

Relative Acidity:

- Formic acid (HCOOH) > Acetic acid (CH_3COOH)
- Chloroacetic acid ($ClCH_2COOH$) > Acetic acid (due to electron-withdrawing Cl)
- Phenol (Ar–OH) < Carboxylic acid (–COOH)
- So, carboxylic acids are weaker than strong mineral acids (like HCl) but stronger than alcohols and phenols.

Structure of Carboxylate Ions

What is a Carboxylate Ion?

- A carboxylate ion is the conjugate base of a carboxylic acid, formed by deprotonation of the –COOH group.

General formula:

$$R–COO^-$$

- Example:
  - Acetic acid (CH_3COOH) → Acetate ion (CH_3COO^-)

Electronic Structure:

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