

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.

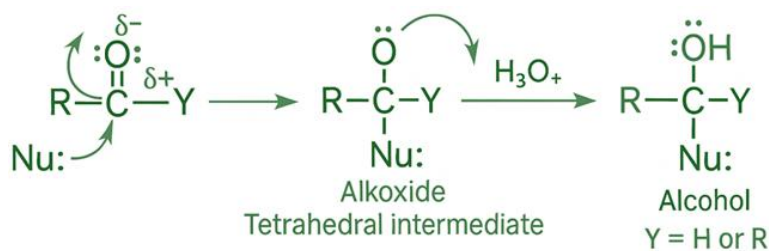
Why It Happens:

- 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

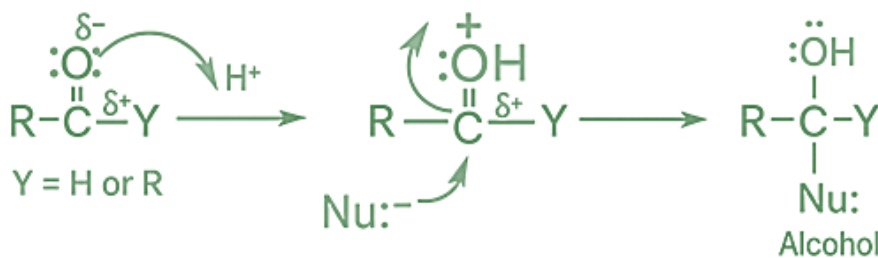
1. Nucleophilic Attack on the Carbonyl Carbon

- A nucleophile (electron-rich species) attacks the electrophilic carbonyl carbon.
- This breaks the π bond of the carbonyl, forming a tetrahedral alkoxide intermediate.



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.



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., H₂O, 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**.



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



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:



Factors Involved:

1. Nature of the –COOH group:

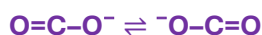
- The carboxyl group has resonance stabilization between the two oxygen atoms in the carboxylate ion, which promotes ionisation.

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.



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:

$$K_a = \frac{[R-COO^-][H^+]}{[R-COOH]}$$

What is pKa?

- pKa is the negative logarithm of Ka:

$$pK_a = -\log K_a$$

- 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:



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

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 $-\text{Cl}$, $-\text{NO}_2$) near the $-\text{COOH}$ 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 $-\text{COOH}$ 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.

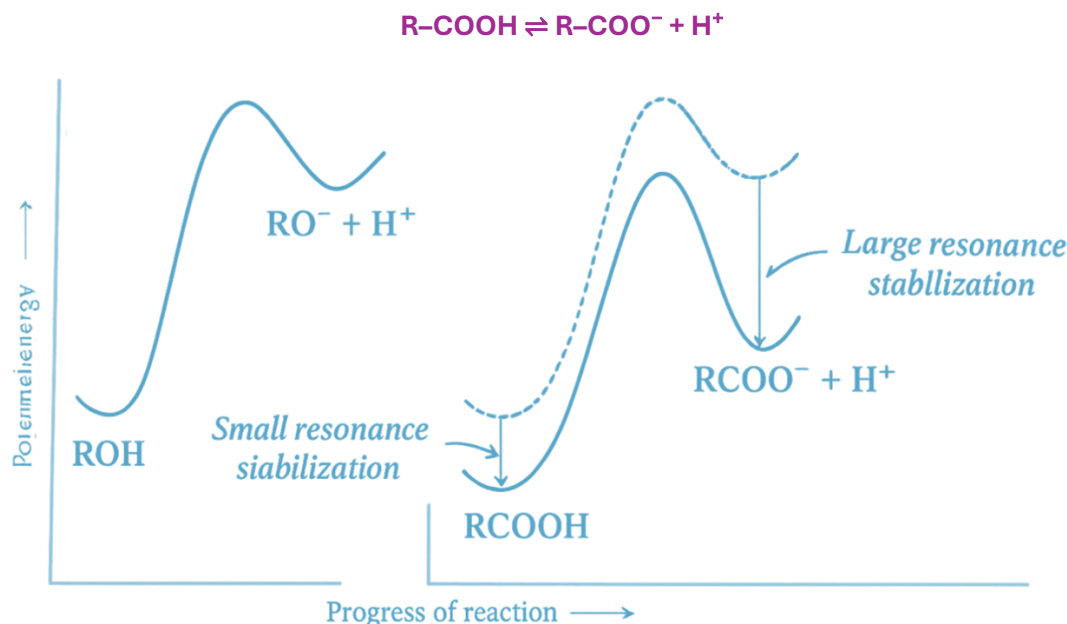
Acidity of Acids

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



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, NO₂) near the –COOH group pull electron density away, stabilizing the negative charge on the carboxylate ion.
- This increases acidity.
- Conversely, electron-donating groups (like CH₃) 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 (CH₃COOH)
- Chloroacetic acid (ClCH₂COOH) > 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:



- Example:
 - Acetic acid (CH₃COOH) → Acetate ion (CH₃COO[–])

Electronic Structure:



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