

SNi, SET, and Neighbouring Group Participation Mechanisms

1. SNi Mechanism (Substitution Nucleophilic Internal)

Definition: Nucleophilic substitution where both the leaving group and nucleophile are part of the same molecule, leading to retention of configuration.

Key Features:

- Unimolecular process (rate \propto [substrate])
- Occurs with retention of configuration
- Internal nucleophile formed during reaction
- Example: Alcohol \rightarrow Alkyl chloride using SOCl_2

Mechanism Example:



Summary: Retention via internal chloride reattack; unimolecular internal nucleophilic substitution.

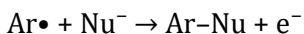
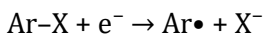
2. SET Mechanism (Single Electron Transfer)

Definition: Involves transfer of one electron from donor to acceptor, forming radical intermediates. Common in photochemical and redox reactions.

Key Features:

- Radical mechanism
- Involves single-electron transfer and radical intermediates
- Occurs in photochemical or metal-free reactions

Example (SRN1 Mechanism):



Applications: SRN1, Sandmeyer, and metal-free borylation reactions.

3. Neighbouring Group Participation (NGP)

Definition: When a nearby atom or group with a lone pair or π -bond participates in the reaction mechanism by forming a temporary bond or cyclic intermediate.

Key Features:

- Neighboring atom assists reaction via anchimeric assistance
- Forms cyclic (bridged) or resonance-stabilized intermediates
- Leads to rate enhancement and altered stereochemistry

Examples:

(a) Participation by lone pair: β -halo ether \rightarrow cyclic oxonium ion intermediate

(b) Participation by π -bond: Allylic or benzylic systems stabilize carbocation

Consequences:

- Rate acceleration
- Possible retention or inversion
- Formation of stable cyclic intermediates

Comparison Summary

S_Ni → Internal substitution (Retention, Ion pair)

SET → Radical mechanism (Single electron transfer)

NGP → Intramolecular assistance (Anchimeric assistance)

Classical and Non-Classical Carbocations, Phenonium Ion, and Reactivity

1. Classical Carbocations

Definition: A classical carbocation is a positively charged carbon species (C^+) in which the positive charge is localized on a single carbon atom.

Structure:

- sp^2 hybridized carbon
- Trigonal planar geometry ($\sim 120^\circ$)
- Contains three σ -bonds and an empty p-orbital

Examples: tert-butyl cation $(CH_3)_3C^+$, benzyl cation $(C_6H_5CH_2^+)$, allyl cation $(CH_2=CH-CH_2^+)$

Stability order: $3^\circ > 2^\circ > 1^\circ > CH_3^+$

Representation: Positive charge is localized on one carbon atom.

2. Non-Classical Carbocations

Definition: A non-classical carbocation is a delocalized carbocation in which the positive charge is shared over two or more carbon atoms by bridging of electrons or σ -bonds.

Structure:

- Involves 3-center-2-electron bonds
- Positive charge delocalized over multiple atoms
- More stable due to delocalization

Examples: Norbornyl cation $(C_7H_{13}^+)$, cyclopropylmethyl cation, phenonium ion.

Key Features:

- Stabilized by delocalization of charge
- More stable than classical cations
- Supported by NMR and X-ray crystallography evidence.

3. Phenonium Ion

Definition: The Phenonium ion is a non-classical benzylic carbocation where the phenyl ring participates in stabilizing the positive charge through formation of a bridged intermediate.

Formation: Occurs during reactions involving β -phenylalkyl halides or aryldiazonium ions:
 $Ph-CH-CH_2-X \rightarrow [Ph-CH-CH_2]^+ \rightarrow$ Phenonium ion.

Structure:

- Three-membered bridged ring between ortho-carbon of phenyl ring and carbocation center.
- Positive charge delocalized between benzylic carbon and aromatic ring.

Significance:

- Explains retention or rearrangement in benzylic systems.
- Intermediate in solvolysis and substitution reactions.

4. Reactivity and Stability of Carbocations

A. Effect of Substrate Structure:

1. Alkyl substitution: +I effect and hyperconjugation stabilize carbocation → $3^\circ > 2^\circ > 1^\circ$.
2. Resonance: Delocalization through π -system → Allyl > Benzyl > Alkyl.
3. Hybridization: $sp < sp^2 < sp^3$ stability.
4. Ring strain relief: Formation of bridged cation increases stability.
5. Neighbouring group participation: Stabilizes carbocation via cyclic intermediate.

B. Effect of Attacking Nucleophile:

1. Strong nucleophile (e.g., OH^- , RO^-): Favors SN2 mechanism.
2. Weak nucleophile (e.g., H_2O , ROH): Favors SN1 mechanism.
3. Bulky nucleophile: Slower attack due to steric hindrance.
4. Polar solvent: Stabilizes carbocation → increases SN1 rate.
5. Aprotic solvent: Stabilizes anions → increases SN2 rate.

Examples:

tert-Butyl bromide + H_2O → SN1 → tert-butyl alcohol

Ethyl bromide + OH^- → SN2 → ethanol

Benzyl bromide → SN1 (fast) → benzyl alcohol

Allyl bromide → SN1 (fast) → allyl alcohol

Summary Table

Classical Carbocation → Planar, localized C^+ ; stability by +I and hyperconjugation (e.g., tert-butyl).

Non-Classical Carbocation → Bridged, delocalized; stability via σ or π delocalization (e.g., norbornyl).

Phenonium Ion → Bridged benzylic; delocalized through aromatic ring (e.g., β -phenylethyl system).