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 → Alkyl chloride using $SOCl_2$

Mechanism Example:
$R{-}CH_2{-}OH \rightarrow R{-}CH_2{-}OSOCl \rightarrow R{-}CH_2{-}Cl$ (retention)
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):
$Ar{-}X + e^- \rightarrow Ar\bullet + X^-$
$Ar\bullet + Nu^- \rightarrow Ar{-}Nu + e^-$
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 → 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

SNi → 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 (~120°)
- 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° > 2° > 1° > 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° > 2° > 1°.
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).