

Summary of Nucleophilic Substitution Reactions

| | S_N1 | S_N2 |
|---|---|---|
| Mechanism | Two Steps $\text{R-L} \xrightarrow{\text{Nu:}} \text{R}^+ \xrightarrow{\text{Nu:}} \text{R Nu}$ | One Step $\text{R L} + \text{Nu:} \rightarrow \text{R Nu}$ |
| Kinetics | 1st order (unimolecular) rate= k [R-L] Ionization = rate determining step (1st step), 2nd step does not affect the rate | 2nd Order (bimolecular) rate= k [R-L] [Nu:] |
| Stereochemistry | Racemization | Inversion |
| Carbon (sp³) Electrophile | Favored by electrophiles which can best stabilize a carbocation. alkyl halide reactivity: 3° > 2° >> 1° | Steric hinderance controlled alkyl halide reactivity: CH ₃ > 1° > 2° no reaction for 3° |
| Nucleophile | Nature of the nucleophile has no affect on rate | Favored by more reactive nucleophiles RS ⁻ > NC ⁻ > I ⁻ > RO ⁻ > HO ⁻ > Cl ⁻ |
| Leaving Groups | Favored by better leaving groups | -OTos > -I > -Br > -Cl > -OH ₂ |
| Solvent Effect | Favored by polar, ionizing solvents. Solvolysis: polar protic (H-bonding) solvents act as the nucleophile | Favored by polar, aprotic solvents. CH ₃ CN > DMF > DMSO Disfavored by polar protic (H-bonding) solvents |
| Competitive Reactions | Elimination (E1) Carbocation rearrangements | Elimination (E2) by strongly basic nucleophiles |