

Summary of Nucleophilic Substitution Reactions

	S _N 1	S _N 2
Mechanism	Two Steps $\text{R-L} \longrightarrow \text{R}^+ \xrightarrow{\text{Nu:}} \text{R-Nu}$	One Step $\text{R-L} + \text{Nu:} \longrightarrow \text{R-Nu}$
Kinetics	1st order (unimolecular) rate= $k[\text{R-L}]$ Ionization= rate determining step (1st step), 2nd step does not effect the rate	2nd Order (bimolecular) rate= $k[\text{R-L}][\text{Nu:}]$
Stereochemistry	Racemization	Inversion
Carbon (sp ³) Electrophile	Favored by electrophiles which can best stabilize a carbocation. $3^\circ > \text{benzylic} \sim \text{allylic} \sim 2^\circ \gg 1^\circ$	Steric hinderance controlled $\text{CH}_3 > 1^\circ > 2^\circ$ ($3^\circ = \text{no reaction}$)
Nucleophile	Nature of the nucleophile has no effect on rate	Favored by better nucleophiles $\text{RS}^- > \text{NC}^- > \text{I}^- > \text{RO}^- > \text{HO}^- > \text{Cl}^-$
Leaving Groups	Favored by better leaving groups $-\text{N}_2 > -\text{OTos} > -\text{I} > -\text{Br} > -\text{Cl} > -\text{OH}_2$	Favored by better leaving groups $-\text{N}_2 > -\text{OTos} > -\text{I} > -\text{Br} > -\text{Cl} >$
Solvent Effect	Favored by polar, ionizing solvents. Solvolysis: polar protic (H- bonding) solvents act as the nucleophile $\text{H}_2\text{O} > \text{H}_2\text{O}/\text{ROH} (\text{mixed solvent}) > \text{ROH}$	Favored by polar aprotic solvents. $\text{HMPA} > \text{CH}_3\text{CN} > \text{DMF} > \text{DMSO} > \text{THF}$ Disfavored by polar protic (H-bonding) solvents
Competative Reactions	Elimination (E1) Rearrangements	Elimination (E2) by strongly basic nucleophiles