Summary of Solvent Effects on Nucleophilic Substitution Reactions

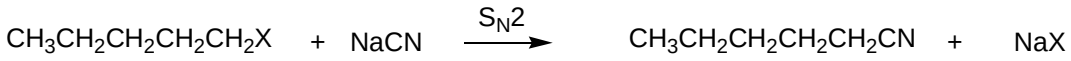
S_N1

- Polar solvent stabilizes transition state and carbocation intermediate.
- Polar protic solvent makes nucleophile less nucleophilic and stabilizes anionic leaving group.

S_N2

- Need polar solvent to dissolve nucleophile.
- Protic solvent slows rate by solvating nucleophile
- Aprotic solvent increases rate by binding cation and thus freeing nucleophile.

Example of effect of solvent on rate of reaction:



reaction 1

X = Br — CH_3OH, 20 h, Δ — 71 %

reaction 2

X = Cl — DMSO, 20 min — 91 %

Summary of S_N1 versus S_N2

S_N1	S_N2
Bond-breaking first (in rate-determining step)	Simultaneous bond breaking and bond forming in rate-determining step
Need stable carbocation (3° R-X)	Need minimal steric hinderance (methyl or 1° R-X)
First order reaction rate	Second order reaction rate
If chiral alkyl halide → racemic product	If chiral → inversion of chiral center
Carbocation rearrangements possible	

If 2° R-X

Polar, protic solvent	Polar, aprotic solvent
Poor nucleophile	Strong nucleophile