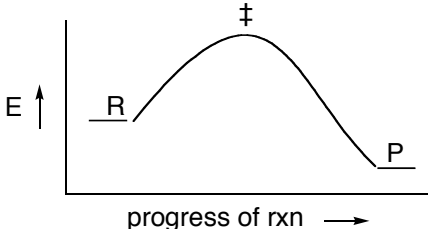
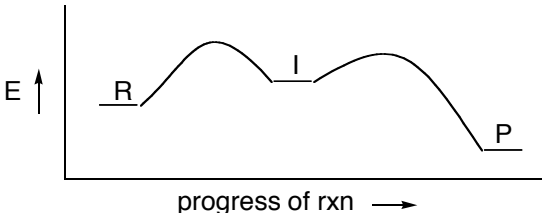
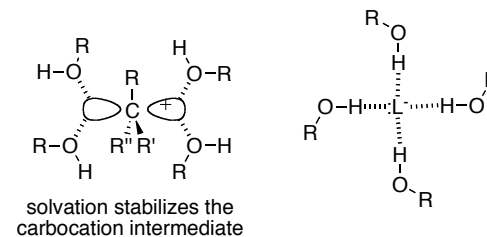
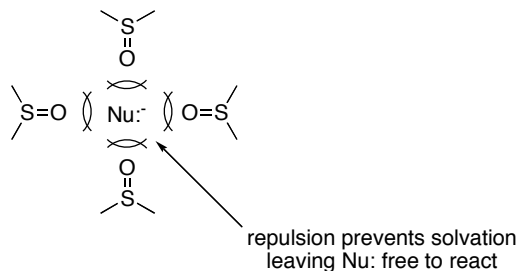


Summary of S_N1 and S_N2 Rxns

Rxn:	<p>S_N2 Rxns (concerted – 1 step)</p> $\text{Nu:}^- + \begin{array}{c} \text{R} \\ \\ \text{R}'''\text{C}-\text{L} \\ \\ \text{R}' \end{array} \longrightarrow \left[\begin{array}{c} \text{R} \\ \\ \delta^- \text{Nu} \cdots \text{C} \cdots \text{L} \\ \quad \delta^+ \quad \\ \text{R}'' \quad \text{R}' \end{array} \right] \longrightarrow \begin{array}{c} \text{R} \\ \\ \text{Nu}-\text{C} \\ \\ \text{R}' \end{array}$	<p>S_N1 Rxns (two steps)</p> $\text{Nu:}^- + \begin{array}{c} \text{R} \\ \\ \text{R}'''\text{C}-\text{L} \\ \\ \text{R}' \end{array} \xrightarrow[\text{slow}]{\text{RDS}} \left[\begin{array}{c} \text{R} \\ \\ \text{C}^+ \\ \\ \text{R}' \end{array} \right] + \text{:L}^- \longrightarrow \begin{array}{c} \text{R} \\ \\ \text{R}'''\text{C}-\text{Nu} \\ \\ \text{R}' \end{array} + \begin{array}{c} \text{R} \\ \\ \text{Nu}-\text{C} \\ \\ \text{R}' \end{array}$
Kinetics:	<p>Rate = k[Nu][R-L] (2nd-order rxn)</p> 	<p>Rate = k[R-L] (1st-order rxn)</p> 
Energy Profile:		
Substrate: (alkyl halide)	<p>1° > 2° > 3° Steric hinderance raises the energy of the transition state and slows the rate of rxn.</p>	<p>3° > 2° ≈ allyl ≈ benzyl > 1° Alkyl groups stabilize the carbocation</p> <p>The more stable the carbocation intermediate, the faster the rate of rxn.</p>
Nucleophile:	<p>More reactive nucleophiles increase the rate of rxn. Good nucleophiles generally are negatively charged (e.g., OH⁻, RO⁻, RS⁻).</p>	<p>Nucleophiles are not involved in the rate determining (slow) first step. Neutral nucleophiles (e.g. H₂O, ROH) often are used for solvolysis, and to reduce E2 elimination.</p>
Leaving Group:	<p>Good leaving groups lower the energy of the transition state and increase the rate of rxn. Good leaving groups are the conjugate bases of strong acids.</p>	<p>Good leaving groups favor formation of a carbocation and increase the rate of reaction. Good leaving groups are the conjugate bases of strong acids.</p>
Solvent:	<p>Polar aprotic solvents (e.g., DMSO, DMF, THF) increase the rate of rxn. These solvents leave the nucleophile unsolvated ("naked") and free to react with the substrate.</p>	<p>Polar protic solvents (e.g., H₂O, ROH, RCO₂H) increase the rate of rxn. These solvents solvate and stabilize both the carbocation intermediate and the leaving group.</p>



Summary of Substitution vs. Elimination

Substitution Favored

1. Weakly basic nucleophiles:
 H_2O , ROH , Cl^- , Br^- , I^- , RS^- , N_3^- , CN^- , RCO_2^-
2. Sterically unhindered haloalkanes:
 1° haloalkanes
3. Sterically unhindered nucleophiles:
 HO^- , CH_3O^- , $\text{CH}_3\text{CH}_2\text{O}^-$, NH_2^-
(substitution may or may not occur)

Elimination Favored

- Strongly basic nucleophiles:
 HO^- , RO^- , NH_2^- , NR_2^-
- Sterically hindered haloalkanes:
branched 1° , 2° , and 3° haloalkanes
- Sterically hindered nucleophiles:
 $(\text{CH}_3)_3\text{CO}^- \text{K}^+$, $[(\text{CH}_3)_2\text{CH}]_2\text{N}^- \text{Li}^+$ (LDA)