**S_N2**
(Substitution of a nucleophile bimolecular)

Mechanism: One step (concerted), nucleophile attacks a sp^3 carbon backside relative to a leaving group, causing inversion of configuration (if appropriate).

\[ \text{NaOme} + \text{MeOH} \rightarrow \text{Ome} \]

**S_N2 Kinetics/Rate law:**
rate = k[haloalkane][nucleophile]

1st order with respect to each substrate but 2nd order (bimolecular) overall

**S_N2 rate factors**
1. High concentrations of haloalkane or nucleophile will increase the rate of reaction
2. Because there is backside attack steric hindrance will slow the reaction down. Therefore, you want the haloalkane to be least sterically hindered (0°<1°<2°) and a small nucleophile.
3. The weaker the base the better the leaving group
   - Tosylates = R-I > R-Br > R-Cl > R-F
4. The stronger the nucleophile the faster the rate
   a. Negative nucleophiles > Neutral nucleophiles
   b. Localized electrons > Delocalized
   c. In aprotic solvents (i.e. DMSO, DMF and acetone) the stronger the base the stronger the nucleophile
d. In protic solvents the larger the nucleophilic atom the stronger the nucleophile. If comparing atoms of comparable size (same period) the stronger the base the stronger the nucleophile.
5. Polarity of the solvent:
   a. Increasing the polarity of the solvent increases the rate for neutral nucleophiles.
   b. Increasing the polarity of the solvent decreases the rate for charged nucleophiles.

**S_N1**
(Substitution of a nucleophile unimolecular)

Mechanism: Two steps, first dissociation of the haloalkane via solvolysis to generate a carbocation intermediate. Second, the nucleophile (typically the solvent) captures the carbocation. Due to the planar geometry of the carbocation the nucleophile has opportunity to attack from either side generating a mixture of configurations (if appropriate).

**S_N1 Kinetics/Rate law:**
Rate = k[haloalkane]

1st order with respect to the haloalkane and 1st order overall (unimolecular).

**S_N1 rate factors**
1. High concentrations of haloalkane. (Note the concentration of the nucleophile has no effect on the rate of an S_N1 reaction.)
2. Due to a late transition state in the slow first step of the mechanism we can expect the transition state to have some carbocation character and therefore the rate would increase as the stability of the carbocation increases. Allylic = 3° > 2°
3. The weaker the base the better the leaving group
   - Tosylates = R-I > R-Br > R-Cl > R-F
4. As the polarity of the solvent goes up the rate of the reaction goes up. (Due to stabilization of the carbocation like transition state.)

Other S_N1 considerations:
1. Possible carbocation rearrangement.
2. Possible resonance for allylic carbocations.