Lecture 2: Nucleophilic Substitution Reactions - SN2 Part 2
Discussion Section Problems Solutions

1. (a) Reaction A:

(b) Crowding depends on the size and number of groups. A hydrogen atom is smaller than a methyl group, so a hydrogen/hydrogen interaction causes less crowding and repulsion than a hydrogen/methyl interaction. Two methyl groups cause a more severe interaction than a hydrogen/methyl interaction. Thus the order of crowding in the transition states is reaction A (three hydrogen/hydrogen interactions; least crowding) < reaction B (three hydrogen/methyl interactions) < reaction C (three methyl/methyl interactions; most crowding).

(c) Energy vs. Reaction coordinate graph showing the energy profiles of reactions A, B, and C.
(d) Crowding raises the energy of the transition state, so more crowding causes a larger $\Delta G^\ddagger$ and a slower reaction. Thus the reaction rates are: reaction A (least crowding; lowest $\Delta G^\ddagger$) > reaction B > reaction C (most crowding; largest $\Delta G^\ddagger$).

(e) Reactions B and C do not occur because their $\Delta G^\ddagger$ values are too high.

We'll learn more about steric hindrance effects on $S_N2$ reaction rate in Lecture 4.

2. (a) In an $S_N2$ reaction, the role of the nucleophile is to share an electron pair with the electrophile.

(b) Stabilizing a nucleophile's electron pair reduces the molecule's nucleophilicity.

3. (a) The nucleophiles differ in their resonance stabilization of the negative formal charge. In general, having more resonance contributors causes more stability.

Nucleophile D has just one significant resonance contributor:

Nucleophile E has five significant resonance contributors:

Nucleophile F has six significant resonance contributors:

Therefore the order of nucleophilicity is: nucleophile D (least number of significant resonance contributors which delocalize the formal charge) > nucleophile E > nucleophile F (greatest number of significant resonance contributors which delocalize the formal charge).
(b) Working off of the basic idea in part (b), we can make nucleophile F even less nucleophilic by increasing the number of formal charge-stabilizing significant resonance contributors. Adding another acyl group (nucleophile G) is one way to achieve this.

Nucleophile G. This nucleophile has seven formal charge-stabilizing resonance contributors, and is therefore less nucleophilic than nucleophile F. Draw out these nucleophile G contributors if you need to convince yourself.

Many other answers are possible.