Lecture 3: Nucleophilic Substitution Reactions - SN2 Part 3  
Discussion Section Problems Solutions

1. (a) (i)  
\[ \text{CH}_3\text{O}^{-} \leftrightarrow \text{CH}_3\text{O}^{-} \leftrightarrow \text{CH}_3\text{O}^{-} \]

(ii)  
\[ \text{PhCO}^{-} \leftrightarrow \text{PhCO}^{-} \leftrightarrow \text{PhCO}^{-} \]

(iii)  
\[ \text{C}_2\text{H}_4\text{O}^{-} \]  
No additional contributors

Having trouble with resonance? Consult these resources:
- Chem 14C notes (second lecture of the course)
- Resonance tutorials (available at the course web site)

(b) **Nucleophilicity**: The role of a nucleophile is to share an electron pair to form a new covalent bond. Any feature that reduces the nucleophile’s ability/desire/driving force to share electrons decreases nucleophilicity. Resonance may delocalize negative charge, resulting in reduced charge density and thus smaller driving force to share electrons. (Reminder: resonance does not always decrease electron density or charge, so it does not always decrease nucleophilicity.) Alternate viewpoint: Resonance is a stabilizing feature. If sharing electrons as a nucleophile reduces resonance then resonance inhibits nucleophilicity.

**Leaving group**: A leaving group should be stable after departure. If resonance adds to this stability, then the group’s propensity to leave is improved. Alternate viewpoint: If departure of the leaving group reduces resonance then resonance inhibits leaving group ability.

2. **Nucleophilicity**: The best nucleophile has the greatest electron density on the atom that it uses to form a new bond with the electrophile. For the given choices, the atom is always oxygen. Some factors that may influence this electron density are discussed below, in order of decreasing importance.

- Resonance: If resonance removes (delocalizes) electron density from the nucleophilic atom, then nucleophilicity is reduced. CH$_3$SO$_3^-$ (methanesulfonate ion) and CF$_3$SO$_3^-$ (trifluoromethanesulfonate ion) both have resonance delocalization but water and hydroxide ion do not. Therefore water and
hydroxide ion are stronger nucleophiles than methanesulfonate ion and trifluoromethanesulfonate ion.

- Atomic radius: Smaller atoms have more concentrated electron density. The nucleophilic atom in all four cases is oxygen, so there is no atomic size difference.

- Electronegativity: Electronegativity is a measure of attraction for electrons. Since a nucleophile’s job is to share electrons, high electronegativity reduces nucleophilicity. The nucleophilic atom in all four cases is oxygen, so there is no electronegativity difference.

- Inductive effect: This is the electron-donating or electron-withdrawing effect of other atoms or groups within the molecule. The three fluorine atoms of trifluoromethanesulfonate ion are highly electronegative, resulting in a strong electron-withdrawing inductive effect. This causes trifluoromethanesulfonate ion to be a poorer nucleophile than methanesulfonate ion.

- Formal charge: This is a measure of electron density relative to the element in its free state. A formal negative charge represents higher electron density. Therefore a nucleophile with a formal negative charge is stronger than a similar nucleophile that is neutral. The relative effect of formal charge is variable. For example sometimes it has more influence than atomic size and sometimes less. Therefore formal charge cannot be placed in a fixed position in our hierarchy of electron density effects.

Considering the factors discussed, we select HO\(^{-}\) as the strongest nucleophile (negative charge, no resonance delocalization, no inductive effect). For the weakest nucleophile we can select either trifluoromethanesulfonate ion (resonance and inductive effect) or water (no formal charge), depending upon what we assume about the relative influence of formal charge in this case.

**Leaving group:** When a leaving group leaves, it accepts the electron pair that used to bond it to the rest of the molecule. The more effectively the leaving group can stabilize this new electron pair, the more eagerly it will leave. This is the reverse of a nucleophile, whose role is to supply an electron pair. We can reason, therefore, that the same electron density effects will influence leaving group ability. In other words, the best leaving group will have the least electron density on the atom that has accepted the electron pair.

Considering the factors discussed under nucleophilicity, we predict the best leaving group to be either trifluoromethanesulfonate ion or water. (In actuality, trifluoromethanesulfonate ion is much superior to water as a leaving group. In fact, CF\(_3\)SO\(_3\)^{-} is one of the very best leaving groups you will encounter). Hydroxide ion is predicted to be the poorest leaving group. *Hydroxide ion is such a poor leaving group that it only*
leaves under certain special circumstances that we will encounter later on in this course. Until then, it is not a leaving group.

(b) \[
\begin{align*}
\text{Ph} & \quad \text{C(CH}_3\text{)}_3 \\
\text{HO} & \quad \text{O} \quad \text{Ph} \\
\text{SO}_2\text{CF}_3 & \quad \text{HO} \\
\text{H} & \quad \text{Ph} \\
\end{align*}
\]

(c) \[
\begin{align*}
\text{HO} & \quad \text{Ph} \\
\text{O} & \quad \text{H} \\
\text{SO}_2\text{CF}_3 & \quad \text{Ph} \\
\text{H} & \quad \text{Ph} \\
\end{align*}
\]

3. (a) \[
\begin{align*}
\text{F} & \quad \text{CH}_2\text{CH}_2\text{Cl} \\
\text{HO} & \quad \text{O} \quad \text{K}^+ \\
\text{HO} & \quad \text{F} \\
\text{O} & \quad \text{CH}_2\text{CH}_2\text{OH} \\
\end{align*}
\]

(b) \[
\begin{align*}
\text{I} & \quad \text{H}_3\text{N} \quad \text{H}_3\text{N} \\
\text{CH}_3 & \quad \text{O} \quad \text{H} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]