S_N2 Solvent Effects Worksheet

The intension of this exercise is to guide you through the logic of figuring out the solvent effect in S_N2 reactions. Take one question at a time; don’t try to think ahead!

This is a good project for your study group, or for individual work.

Consider this general S_N2 reaction:

\[ \text{Nuc}^- + R_3C-LG \rightarrow \text{Nuc} \rightarrow CR_3 + LG^+ \]

1. Are the nucleophile (Nuc) and the transition state polar or nonpolar?

2. Which solvent is best at stabilizing the nucleophile and transition state? Polar or Nonpolar?

3. Explain your choice in question #2. (“Like dissolves like” is not acceptable. Think about the dielectric constants of the polar solvent and nonpolar solvent, and how they reflect in the solvents’ ability to solvate the nucleophile and transition state.)

4. Consider the use of polar solvent:
   (a) But first, do the nucleophile and the transition state have the same net dipole moment? (Keep in mind the answer while answering the questions below.)
   (b) From a scale of -10 → 0 → 10 (-10 = most destabilized, 10 = most stabilized), how much stabilization/destabilization does polar solvent provide to the nucleophile? Remember this exercise is qualitative, not quantitative.
   (c) Again, from a scale of -10 → 0 → 10, how much stabilization/destabilization does the polar solvent provide to the transition state?
   (d) Now, translate your answers in part a) and b) into an energy diagram. Provided below is an energy diagram for the same reaction using a “universal solvent”. Remember stabilization = lowering energy and destabilization = raising energy.

(e) How does the polar solvent affect activation energy (the energy difference between the reactants and transition state) of this reaction? Does the reaction proceed faster or slower in polar solvent?

5. Consider the use of nonpolar solvent in this question. Answer similar sub-questions as in question #4, but for nonpolar solvent.

6. Consider your answers in 3d) and 4d), which solvent would you pick for this S_N2 reaction? Polar or nonpolar? Why? If you have a choice to use a different solvent, what would you choose?
**Break:** If your answer in question #5 is moderately polar, give yourself a pat in the back and move on. If not, still give yourself a pat in the back for trying, then ask for clarification on the course discussion board, in discussion section, or during office hours.

**Note:** When deciding on a solvent for $S_N2$ reaction, remember to consider the charge state of the nucleophile and the transition state. Evaluate the effect the solvent has on each one, but the net effect is what matters.

7. What is a protic solvent? What is an aprotic solvent?

8. Consider the same $S_N2$ reaction in protic solvent:
   (a) In what way does the protic solvent interact with the nucleophile?
   (b) Does it stabilize or destabilize the nucleophile?
   (c) Does it enhance or diminish the ability of the nucleophile to share electrons? What does it mean to the nucleophilicity?

9. How about the same reaction in aprotic solvent? Answer the same sub-questions in #7 but for aprotic solvent.

10. What solvent would you pick for an $S_N2$ reaction, protic or aprotic?

11. Shown below are the energy diagrams for the $S_N2$ reactions where $F^-$ and $I^-$ are the nucleophiles. The reactions proceed in DMF, an aprotic solvent.

   ![Energy Diagrams](image)

   (a) Which one is a better nucleophile in DMF, $F^-$ or $I^-$?
   (b) When the reactions are run in methanol, a protic solvent, does the energy of $F^-$ increase or decrease? What about for $I^-$?
   (c) Does methanol increase/decrease the energy of both nucleophiles by the same amount? Why or why not?
   (d) Qualitatively, draw the new energy diagrams for both nucleophiles in methanol.
   (e) Which nucleophile is more affected by this change in solvent?
   (f) Which one is a better nucleophile in methanol, $F^-$ or $I^-$?
S_N2 Solvent Effects Worksheet - Solutions

1. Polar

2. Polar

3. Polar solvent has higher dielectric constant than nonpolar solvent. Higher dielectric constant means better at solvating polar bonds, charges. So polar solvent is better at solvating polar nucleophile and polar transition state.

4. (a) No
   
   (b) 8

   (c) 3 Your exact answers for (b) and (c) do not matter as long as the value in (b) is greater than the value in (c).

   (d) Increase activation energy. Slower.

5. (a) No
   
   (b) -8

   (c) -3 Your exact answers for (b) and (c) do not matter as long as the absolute value in (b) is greater than the absolute value in (c).

   (d) Decrease activation energy. Faster.

6. Polar solvent. Even though polar solvent makes the reaction proceed slower, nonpolar solvent does not solvate polar reagent. (Better to have a slow reaction than no reaction at all). Moderately polar is best in this case.
7. Protic solvent is a hydrogen bond donor. Aprotic solvent cannot donate a hydrogen atom for a hydrogen bond. **Review these definitions at the Illustrated Glossary of Organic Chemistry on the course web site.**

8. (a) Protic solvent hydrogen bonding with the nucleophile.

   (b) Stabilize the nucleophile.

   (c) Diminish. Decrease nucleophilicity of the nucleophile.

9. (a) Does not interact significantly with the nucleophile.

   (b) Neither

   (c) Neither. Does not significantly affect nucleophilicity.

10. Aprotic

11. (a) $F^-$

    (b) Decrease. Same for $\Gamma^-$

    (c) No. Methanol stabilizes $F^-$ more than $\Gamma^-$ because $F^-$ is smaller in atomic size, has denser electron cloud; forms stronger hydrogen bond with methanol than does $\Gamma^-$. 

![Diagram](image-url)