Contents

Week x	
Tueday, November 17 - Quiz 19	2

Week x

Tueday, November 17 - Quiz 19

- 1. In an S_N 2 reaction in which OH⁻ is the nucleophile, in which solvent will the rate will the rate (be) the fastest?
 - > a polar aprotic solvent
 - a nonpolar solvent
 - ▷ a polar protic solvent
 - ▶ Polar aprotic solvents: protic solvents lacking a hydrogen atom connected to electronegative atoms.
 - Lack of hydrogen fails to stabilize added nucleophiles, leaving compounds with higher potential energy and thus a lower activation energy for a reaction to take place.
 - \circ S_N 2 reactions are generally much faster in polar aprotic solvents.
- 2. The carbon center in a alkyl halide is
 - > an unsaturated center
 - ▷ a nucleophile
 - ▷ a cation
 - > an electrophile
 - ▶ **Alkyl halides**: compounds in which a halogen (Cl, Br, I) is connected to sp^3 hybridized carbon atom.
 - Alkyl halides are electrophiles since they contain such electron deficient halogens—making them easily accept new electrons.
- 3. Why is the rate of reaction for an S_N 2 reactions so much slower for a 3° alkyl halide than for a 1° alkyl halide?
 - ▶ the leaving group is more reactive in an 1° alkyl halide
 - steric crowding is much less in 3° alkyl halldes
 - \triangleright because $\triangle G^{\circ}$ is much smaller for a 3° alkyl halide

 - ▶ The more substituents, the more bonds that need to be broken/changed and the more steric intereactions there are during the transition state—leading to higher activation energy and thus a slower reaction.
 - Steric crowding refers to the steric intereactions that act to increases such interference.
 - \circ 3° refers to the number of of β positions (max 3°, min 1°)

- α **position**: the position connected directly next to the halogen.
- β **position**: positions connected to the α position.
- 4. At the transition state of an S_N 2 reaction reaction
 - b the C−Nu bond is partially formed and the C−LG bond is partially broken.
 - ▶ the C−Nu bond is *partially* formed and the C−LG bond is *completely* broken.
 - b the C−Nu bond is completely formed and the C−LG bond is partially broken.
 - b the C−Nu bond is partially formed and the C−LG bond is completely intact.
 - > **Transition states**: represent local maxima of the reaction.
 - Cannot be isolated.
 - Represents high-energy states where bonds are being simultanesously broken and formed.
 - I.e., partially broken and partially formed.
- 5. The rate law expression for an S_N 2 reactions reaction has the form
 - \triangleright rate = k[electrophile]
 - \triangleright rate = $k[electrophile]^2$
 - rate = k[nucleophile]²
 - ▶ rate = k[electrophile][nucleophile]
 - \triangleright **Kinetics of** S_N 2 **reactions**: a biomolecular (2) nucleophilic (N) substitution (S) reaction.
 - Biomolecular: a step that involves two chemical entities, such as when the alkyl halide and nucleophile collide during the reaction mechanism.
 - Rate: $v_0 = k$ [alkyl halide][nucleophile]
 - As mentioned above, alkyl halides are electrophiles.

- 6. What is the meaning of S_N 2?
 - > substitution nucleophilic two transition states

 - **> substitution nucleophilic two second order**
 - > substitution nucleophilic two twice
 - \triangleright Rate = $k[A]^x[B]^y$
 - Rate order: the sum of exponents of the reactants.
 - E.g., kA = first, kAB = second, $kA^2B = \text{third}$.
- 7. Which would you expect to be the best nucleophile?
 - ⊳ F
 - > (CH₃)₂CH⁻
 - \triangleright CH₃
 - ⊳ (CH₃)₃C⁻
 - ▶ **Nucleophilicity**: the rate at which a nucleophile will attack a suitable electrophile.
 - There are multiple factors that contribute, but three main factors at play here: the role electron density, electronegativity, and steric hinderance (crowding).
 - $(CH_3)_2CH^-(2^\circ)$ and $(CH_3)_3C^-(3^\circ)$ have more β branching, thus more hinderance.
 - F electron density is so small that it causes low polarizability (more sable), which reduces reactivity.
 - Nucleophilicity also decreases as electronegativity increases (F > O > N > C), so carbon will be have higher Nucleophilicity.
- 8. In substitution reactions with alkyl halides,
 - ▶ the nucleophile is the leaving group
 - ▷ a hydrogen becomes the leaving group
 - **b** the halide is the leaving group
 - ▶ the electrophile is the leaving group
 - ▶ I an alkyl halide, the halogen serves two critical functions that render the alkyl halide reactive:
 - The halogen withdraws electron density via induction, rending the adjacent carbon atom electrophilic, and therefore subject to attack.

- The halogen can serve as the leaving group for the compound, vital for substitution or an elimination to occur.
 - Good leaving groups are conjugate bases of strong acids, i.e., good groups are weak bases.
 - Generally an acid with a $pK_a < 0$ generates a stable enough base to be a good leaving group, which is another reason why F (pK_a of HF is 3.2) is not one, despite being a halogen.
- 9. Of the following, which is the better nucleophile?
 - > H₂O
 - ⊳ NH₃
 - ⊳ RNH⁻
 - $\triangleright NH_2^-$
 - ▶ This question has more to do with the solvent effects on nucleophilicity.
 - **Protic solvents**: polar solvent that contains a hydrogen atom connected directly to an electronegative atom.
 - Polar aprotic solvents: protic solvents lacking a hydrogen atom connected to electronegative atoms.
 - Both H₂O and NH₃ have are protic solvents, with hydrogen on the electronegative oxygen and nitrogen.
 - \triangleright Comes down to RNH⁻ and NH₂⁻.
 - I believe the R is a functional group, which shares more of the negative charge, decreases strength relative to NH₂⁻
 - Although, I'm not completely sure, and I welcome a better explanation.