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### Week 8

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1. What is the rate law for an  $S_N1$  reaction of an alkyl halide?
  - ▷ rate =  $k[\text{alkyl halide}]^2$
  - ▷ **rate =  $k[\text{alkyl halide}]$**
  - ▷ rate =  $k[\text{nucleophile}]$
  - ▷ rate =  $k[\text{alkyl halide}]$
  - ▷ Unimolecular:  $S_N1$  and E2 reactions that are linearly dependent on the concentration of only one compound (the substrate).
  - ▷ A first order rate:  $v_0 = k[\text{substrate}]$ 
    - The substrate varies, and can be more than just an alkyl halide, but alkyl halides are very common.
2. What is the rate limiting step for an  $S_N1$  reaction?
  - ▷ **formation of carbocation**
  - ▷ loss of an  $H^+$  ion from the nucleophile
  - ▷ backside attack of the nucleophile
  - ▷ The alkyl halide often acts as the rate-determining step for  $S_N1$  reactions.
    - I think the better answer would be that the loss of the alkyl halide (leaving group) acts as the rate-determining step, but the loss of the leaving group is what forms the carbocation.
  - ▷  $S_N1$  reactions are often just two-steps (formation of carbocation → nucleophilic attack), but the transfer of an  $H^+$  can occur if the nucleophile is uncharged, which is done by a solvent molecule.
3. Which reaction proceeds with an inversion of configuration?
  - ▷  $S_N1$
  - ▷  **$S_N2$**
  - ▷ acid base reactions
  - ▷ addition reactions
  - ▷  $S_N2$  reactions always invert, but technically both  $S_N1$  and  $S_N2$  reactions can do so as well.
  - ▷ If the halogen in a  $S_N1$  reaction is bonded to an asymmetric center then it produces a pair of enantiomers, one of which will be inverted.

- This is because the nucleophile can attack the carbocation in either direction.
  - Note: observation evidence shows a there is sometimes a slight preference for the inverted product, probably due to the type of ion pairs created.
4. Which conditions are most favorable an  $S_N1$  reaction?
- ▷ a bulky nucleophile and a  $1^\circ$  alkyl halide
  - ▷ a bulky nucleophile and a  $2^\circ$  alkyl halide
  - ▷ **a bulky nucleophile and a  $3^\circ$  alkyl halide**
  - ▷ a small unhindered nucleophile and a  $1^\circ$  alkyl halide
  - ▷ Primary and secondary alkyl halides don't undergo  $S_N1$  reactions. The carbocation needs to be stabilized (hyperconjugation), and can need the most stable form ( $3^\circ$ ) in order to do so.
5. For either an  $S_N1$  or an  $S_N2$  reaction, which is the best leaving group?
- ▷  **$I^-$**
  - ▷  $F^-$
  - ▷  $Cl^-$
  - ▷  $Br^-$
  - ▷ Alkyl iodides are the most reactive, while fluorides are the least.
    - $I^- > Br^- > Cl^- > F^-$
  - ▷ This is in large part determined by **polarizability**, which **increases with size of atom** since electrons occupy more space around the atom and thus have a higher chance of randomly forming differences in charge due to uneven distribution of electrons.
6. Why is a tertiary carbocation so much more stable than a primary carbocation?
- ▷ steric bulk helps stabilize the tertiary carbocation
  - ▷ **hyperconjugation provides more stability in a tertiary carbocation than in primary carbocation.**
  - ▷ a tertiary carbocation is more stabilized by the leaving group
  - ▷ a tertiary carbocation is more ideal trigonal planar geometry
  - ▷ **Hyperconjugation:** nearby electron sharing of electrons with adjacent empty, or partially filled orbitals, that give rise to more stability.
  - ▷ A primary carbocation has no such orbitals to share with, so the instability is increased.

7. According to the Hammond Postulate, the transition state for a reaction that proceeds with a large activation energy
- ▷ will be more likely to go by an  $S_N2$  pathway
  - ▷ **looks more like the products**
  - ▷ will be more likely to go by an  $S_N1$  pathway
  - ▷ looks more like the reactants
  - ▷ A higher energy transition state (larger activation energy) means it takes more energy to make any sort of change at all, which means change occurs rapidly once it finally can—creating transition states that look more like the products.
    - This is why they are **endothermic**; more energy is required, resulting in more energy **entering** the system from the outside.
    - This also explains why the products are less stable; more energy remains in the system due to these products.
8. The choice of a solvent affects the rate of the reaction by
- A changing the stability of the reactants
  - B changing the stability of the transition state
  - C changing the stability of the products
  - ▷ all of the above
  - ▷ **A and B**
  - ▷ The choice of solvent, often protic or aprotic, changes the stability of the added nucleophiles (increasing/decreasing respectively).
  - ▷ Stronger, less stable nucleophiles increase the potential energy in the reaction, which decreases the activation energy. The inverse is true for weaker, more stable
  - ▷ A change the activation energy often results in different products being formed, which usually differ in stability, but this does not affect the rate.