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Week x

Tueday, November 17 - Quiz 19

1. In an S_N2 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.
        - S_N2 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 sn 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_N2 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 halides
    - ▷ because $\Delta G°$ is much smaller for a 3° alkyl halide
    - ▷ **steric crowding is much greater in 3° alkyl halides**
    - ▷ 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.
        - 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_N2 reaction reaction
    - ▷ **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.
    - ▷ the C—Nu bond is *completely* formed and the C—LG bond is *partially* broken.
    - ▷ the C—Nu bond is *partially* formed and the C—LG bond is *completely in tact*.
    - ▷ **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_N2 reactions reaction has the form
    - ▷ rate = k[electrophile]
    - ▷ rate = k[electrophile]^2
    - ▷ rate = k[nucleophile]^2
    - ▷ **rate = k[electrophile][nucleophile]**
    - ▷ **Kinetics of S_N2 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_N2?
    - ▷ substitution nucleophilic two transition states
    - ▷ substitution nucleophilic two two reagents
    - ▷ **substitution nucleophilic two second order**
    - ▷ substitution nucleophilic two twice
    - ▷ Rate $=k[A]^x[B]^y$
        - **Rate order**: the sum of exponents of the reactants.
            - E.g., $kA =$ first, $kAB =$ second, $kA^2B =$ third.
7. Which would you expect to be the best nucleophile?
    - ▷ F^-
    - ▷ $(CH_3)_2CH^-$
    - ▷ **CH_3^-**
    - ▷ $(CH_3)_3C^-$
    - ▷ **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°) and $(CH_3)_3C^-$ (3°) 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
    - ▷ **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?
   - ▷ H_2O
   - ▷ NH_3
   - ▷ RNH^-
   - ▷ **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 H_2O and NH_3 have are protic solvents, with hydrogen on the electronegative oxygen and nitrogen.
   - ▷ Comes down to RNH^- and NH_2^-.
     - I believe the R is a functional group, which I assume adds a greater degree of polarizability due to spread of electron density.
     - Although, I'm not completely sure, and I welcome a better explanation.