CHEM 261

Substitution Reactions

S_N1 reactions - Substitution Nucleophilic Unimolecular

- Rate depends on 1 concentration (concentration of the starting material)
- Not concerted has a carbocation intermediate (stepwise reaction)
- Not stereospecific
- Works if leaving group is tertiary (not primary, slow on secondary)

Example: Tertiary Halide

-No S_N2 possible, sterically crowded - does work by S_N1



S_N1 Energy Diagram

E.g.



Mechanism:

The bromine group leaves with its electrons from the covalent bond, leaving behind a reactive carbocation intermediate



Carbocation Stability:



donate e⁻ density into the positive charge

Mechanism of Nucleophilic Attack on Carbocation



sp³, tetrahedral, bond angle 109°

The result of an S_N1 mechanism is often a racemic mixture or mix of diastereomers

• S_N1 reactions run under acidic conditions (basic conditions will undergo elimination)

Photosynthesis and Related Reactions



• Plants consume $4x10^{11}$ metric tons of CO₂ per year and convert it to D-Glucose



Hydrogen iodide is a strong acid and will drive the reverse reaction, meaning the forward reaction will not occur.

In order to make the above reaction occur, a stronger base (such as sodium methoxide) must be used to drive the forward reaction.



Example:



The above reaction will not occur unless hydrogen cyanide is converted into sodium cyanide using NaOH.

The product is acetonitrile, a common laboratory solvent.

<u>REVIEW</u>: S_N2 yes or no ? Examples



Ex #4) The one below does NOT work

 $\overset{\bigcirc}{OH}, \overset{\bigcirc}{OR}, \overset{\bigcirc}{NR}_2$ are never good leaving groups



In this reaction, the NH_2 species will pull off the most acidic proton (the one on the alcohol) to from an **alkoxide** instead of undergoing an $S_N 2$ reaction.

S_N1 and S_N2 Examples:

Ex #1)



Mechanism:

