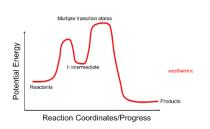
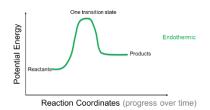
Major Concepts Covered from Videos 30-33:

Reaction pathways

Step-wise reaction

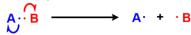
Concerted (one-step) reaction

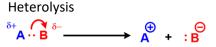




Bond cleavage and formation

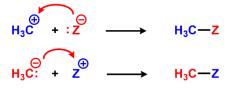
Homolysis





Bond formation

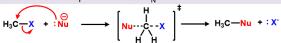
NUCLEOPHILE – electron rich species (seeks a positive center) **ELECTROPHILE** – electron deficient species (seeks e⁻ to fill octet)



Nucleophilic substitution mechanisms

Two nucleophilic substitution (SN) reaction mechanisms

A: The nucleophilic attack and the leaving group departure occurs in one-step: Concerted: $S_{\rm N}2$



transition state

B: Reactants converted to products via more than one step: $S_N 1$ Step 1: Heterolytic **cleavage** of C-X bond – carbocation formed Step 2: Then nucleophile attacks the electrophile

$$R - C = X + \begin{bmatrix} R \\ R \end{bmatrix} + \begin{bmatrix} R - C \\ R \end{bmatrix} + \begin{bmatrix} R - C \\ R \end{bmatrix} + \begin{bmatrix} R \\ R$$

Electrophilic addition to alkenes

ELECTROPHILE – hydrogen of H-X (or other δ + of x-X reagent) **NUCLEOPHILE** – "attacking" π bond

Markovnikov's rule: hydrogen adds to the carbon in the double bond that has more hydrogen atoms, and the halogen adds to the carbon with fewer hydrogen atoms

Elimination mechanisms

Two elimination (E) reaction mechanisms

1: Bond breaking and bond formation occur one-step: E2

2: Reactants converted to products via more than one step: E1 Step 1: Heterolytic cleavage of C-X bond – carbocation formed Step 2: Nucleophile attacks the electrophile

Question 1. Label each reaction event below with either the bonding-breaking type or the specific reaction type. Choose the type that <u>best</u> describes the reaction event drawn.

Choices: substitution, addition, elimination, heterolytic cleavage, homolytic cleavage

Reaction scheme	Reaction type (one best choice)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
: CI CI: 2 · CI:	
+ HCN - OH	
H_CI	

Question 2. Break the red bond of the following molecules in either a homolytic or heterolytic fashion, as indicated. Show the cleaved products produced with the appropriate electrons and charge. Be sure to draw in the correct arrows to show the movement of electrons.

a)
:Br—Br: —
Homolytic cleavage
:Br:
Heterolytic cleavage
O—O CH ₃
Homolytic cleavage
CI
Heterolytic cleavage

Question 3. Answer the questions below based on the following reaction energy diagram

Reactants — [Intermediate] — Products

Step A | Step B |

Intermediate |

Reactants |

Products |

Reaction progress

- i. Is the reaction concerted or stepwise?
- ii. Is the reaction endothermic or exothermic overall?
- iii. How many transition states are there in this reaction pathway?

Question 4. Identify the mechanism below as either S_N1 , S_N2 , E2 or E1. Circle the leaving group in each reaction. Put a square around the nucleophile.

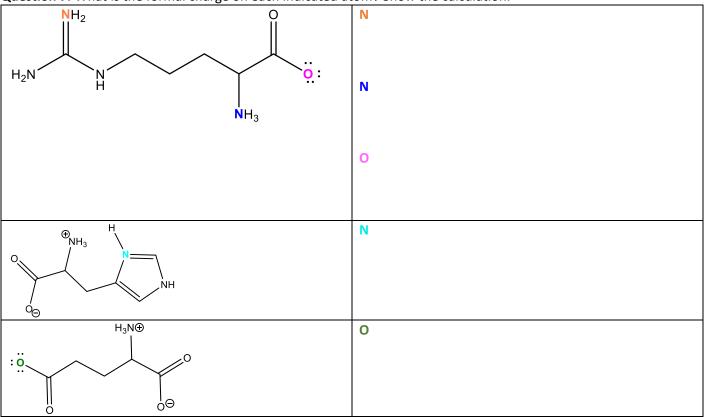
Reaction mechanism	Mechanism type
:OH⁻ + H−C−Br: → :Br: + H₃C−OH	
$H \xrightarrow{H} \xrightarrow{H} \xrightarrow{H} \xrightarrow{H} \xrightarrow{C} \xrightarrow{C} \xrightarrow{H} + CI^{-} \xrightarrow{OH^{-}} \xrightarrow{H} \xrightarrow{H} = C \xrightarrow{H} + H_{2}O + : CI^{-}$	

Question 5. Draw the mechanism of reaction and the product formed resulting from an $\underline{E1}$ reaction of the following reactant and substrate:

Question 6. a) Provide the detailed mechanism of the SN2 reaction of methylchloride with sodium hydroxide. Include any transition states or intermediates of the reaction. Use arrows to indicate the flow of electrons and indicate any charge/lone pairs that are important.

b) Assume that the SN2 reaction above is exothermic, draw the associated reaction energy diagram for this reaction. Include all the necessary labels.

Question 7. What is the formal charge on each indicated atom? Show the calculation.



Question 8. Draw the product(s) of the arrow pushing.

Question 9. Draw the products of the reactions.

In class review (November 21 and 22)

Question 10. Which is the better nucleophile from each pair and why?