Activity 8 Polar Mechanisms

Focus Question

What are some factors that we must consider in order to draw reasonable polar mechanisms?

Model 1

Some General Mechanistic Rules

A) Leaving Groups

For S_N1, S_N2, E1 and E2 reactions, there are a limited number of groups that can act as leaving groups: *chloride, bromide, and iodide anions, and derivatives of sulfate anions*

For acid-catalyzed S_N1 and E1 reactions: *water and alcohols*

For S_N2 and E2 reaction in strongly acidic or strongly basic conditions: *ethers*

For reactions in which a negatively charged atom, which is already attached to the carbon with the leaving group, forms a π bond when the leaving group leaves: *Any species other than a hydride or hydrocarbon anion.*

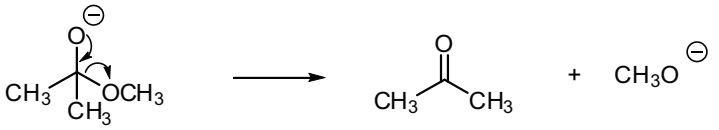
B) Acidic and basic reactions

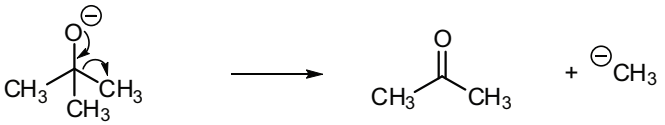
A reaction mechanism will not contain any species with a negatively charged carbon, nitrogen, or oxygen unless the reactants include a negatively charged carbon, nitrogen, or oxygen (with the exception of cyanide ion). Also, a reaction in which the reactants contain a negatively charged carbon, nitrogen, or oxygen will not occur via any step that contains a positive charge on one of those atoms.

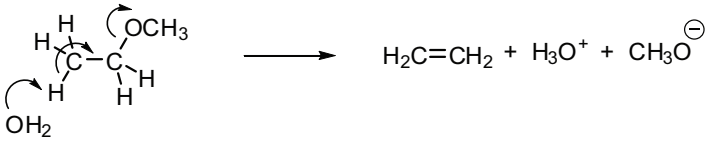
C) Number of species reacting in one step

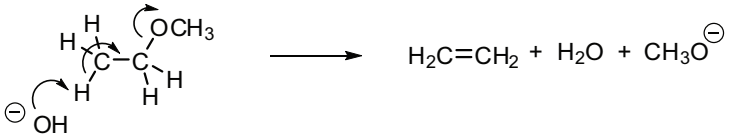
The probability that three separate species will come together simultaneously in the correct orientation for a reaction to occur is very small, so each step in a mechanism must have at most two species reacting.

1. Cross out the following reaction steps that violate any of the rules in Model 1.

a. 

b. 

c. 

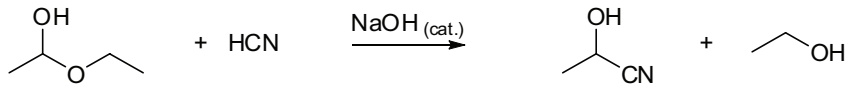
d. 

2. For each reaction step you crossed out in the previous question, explain which rule it violates.

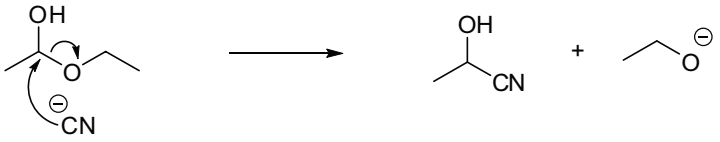
Model 2

Drawing Mechanisms

Consider the following reaction:



A possible mechanism:



3. From where would CN^- come? Draw out this reaction.

4. What type of mechanism is shown?

5. Can ethoxy act as a leaving group in this type of mechanism? Base your answer on the rules in Model 1.

6. Is this a reasonable mechanism for this reaction? Explain.

7. Under the given reaction conditions, will the oxygen of the ether be protonated? Explain your reasoning.

8. Is it possible for this reaction to occur via an S_N2 mechanism? Explain your reasoning.

9. Obviously, the ethoxy group must leave some point for the products to be formed in this reaction. This group will not be protonated before it leaves because the reaction conditions are not acidic enough. According to the rules in Model 1, what is the only type of reaction in which this ethoxy group can act as the leaving group?

10. Propose an intermediate from which, according to the rules, the ethoxy group can leave.

11. Propose a step in this mechanism leading to the intermediate you drew for question 10 that can immediately follow the initial acid base reaction between hydroxide and cyanide gas.

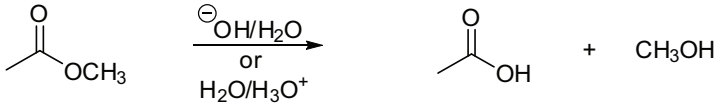
12. Draw out the remaining steps to complete the mechanism.

13. Check that each step in your mechanism does not violate any rules in Model 1.

Model 3

Hydrolysis of Esters

The hydrolysis of an ester, a nucleophilic substitution at a carbonyl carbon, can be catalyzed by either acid or base. This reaction has a multi-step mechanism.



14. One of the steps involves the nucleophile attacking the carbonyl carbon. What acts as the nucleophile in the base-catalyzed reaction? In the acid-catalyzed reaction?

15. Another step involves the leaving group leaving. What acts as the leaving group in the base-catalyzed reaction? In the acid-catalyzed reaction?

16. Draw out the entire mechanism for the base-catalyzed reaction in Model 3. Make sure that each step conforms to the mechanistic rules in Model 1.

17. Draw out the entire mechanism for the acid-catalyzed reaction in Model 3. Make sure that each step conforms to the mechanistic rules in Model 1.

18. Describe in words the major differences between the mechanism of an acid-catalyzed ester hydrolysis and that of a base-catalyzed one.

EXERCISE

Propose a reasonable mechanism for the following 4-step reaction.