ChemActivity 31  Nucleophilic Addition to a Carbonyl

Part A: Nucleophilic Addition to C=O
(What is the mechanism by which a aldehyde or ketone can be converted to an alcohol?)

Review
nucleophile = “nucleus (+) lover”  nucleophilic = “nucleus (+) loving”
electrophile = “electron (-) lover”  electrophilic = “electron (-) loving”

Model 1: Nucleophilic Addition with a Very Strong Nucleophile

Critical Thinking Questions
1. Draw a δ+ and a δ- on appropriate atoms of formaldehyde to show the polarity of the C=O bond.

2. Use curved arrows to show a mechanism for the reaction in Model

3. Draw the alcohol product that results when an aldehyde or ketone is
   i) treated with a Grignard or Lithium reagent (strong nucleophile)
   ii) then neutralized with dilute acid

4. According to the following factors, which do you expect to be more susceptible to reaction with a nucleophile: the carbonyl carbon of an aldehyde or a ketone?
   i. Based on sterics, which is more reactive: aldehyde C or ketone C?
   ii. Based on electronics, which is more reactive: aldehyde C or ketone C?
      (Hint: recall that alkyl groups are electron donating.)

example of an aldehyde (propanal)  example of an ketone (2-butanone)
Model 2: Nucleophilic Addition with a Weak Nucleophile

Under normal conditions, most aldehydes and ketones are stable in water. However, when a small amount of acid is added as a catalyst, a di-alcohol product called a hydrate forms.

Critical Thinking Questions

5. Use curved arrows to construct a mechanism for the reaction in Model 2 such that no intermediate has a negative charge on H, C or O.
   Hint: the acid catalyst is involved in the first step.

6. The first intermediate in the reaction above has two resonance forms. Draw the other resonance structure of this intermediate.
Model 3A: Singles Dance *circa* 1930

The singles dance where my grandparents met provides a model for understanding how a system at equilibrium responds to stresses like adding more reactants, or taking away products. There were about 300 singles at the Synagogue that evening: roughly 200 men and 100 women. (Gramps beat the odds!) Because of teen shyness and limited space on the dance floor, by eight o’clock only 50 male-female dance couples had formed.

**Starting Conditions**

<table>
<thead>
<tr>
<th>200 single men</th>
<th>100 single women</th>
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**After the system has come to equilibrium**

<table>
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<tr>
<th>150 unreacted men</th>
<th>50 unreacted women</th>
<th>50 couples</th>
</tr>
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**Critical Thinking Questions**

7. At 9:00pm, a busload of 100 more single men arrived, and soon after there were 70 male-female couples crammed onto the dance floor. Construct an explanation for this new equilibrium position.

8. How many male-female couples do you expect on the dance floor if 1000 single men showed up (instead of 100 single men)?

9. Did the addition of men cause the reaction (shown with arrows in Model 3) to go forward (from left to right) or go backwards (right to left).

Model 3B: Le Chatelier’s Principle

French chemist Henri Louis Le Chatelier (1850-1936) noticed that a system in equilibrium responds to stress by trying to move back toward equilibrium.

**Critical Thinking Questions**

10. Applying Le Chatelier’s principle to the singles dance in Model 3A, what would you expect to happen if (instead of any men arriving) a bunch of couples left at 9pm—creating space on the dance floor.
11. Imagine a hypothetical chemical reaction in equilibrium:

\[ A + B \rightleftharpoons C + D \]

For each stress, state whether the reaction will go forward or backward or neither.

- a. add more A.
- b. add more D
- c. take away some D
- d. take away some B
- e. add more A and more B
- f. add more A and take away a similar amount of D
- g. add more C and add a similar amount of B

12. Consider an energy diagram for the overall reaction from Model 2 (shown below). Because the reaction is neither up-hill nor down-hill in energy, at equilibrium, you would expect a 1:1 ratio of aldehyde to hydrate.

According to Le Chatelier's Principle, we can control the final equilibrium ratio of aldehyde to hydrate by...

- adding water or removing water.

Which of these actions will shift the equilibrium toward more aldehyde and which will shift the equilibrium toward more hydrate? Explain.