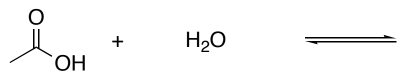
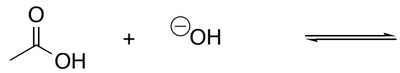
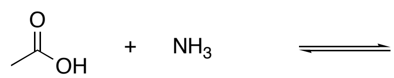
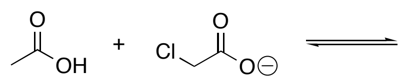
Chem 2062 Spring 2006
Ch 20 Group work

1. Predict the products of the following acid/base reactions, then decide which direction the equilibrium lies. (Hint, find the stronger acid.) Briefly explain your answer:

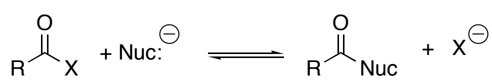
a. 

b. 

c. 

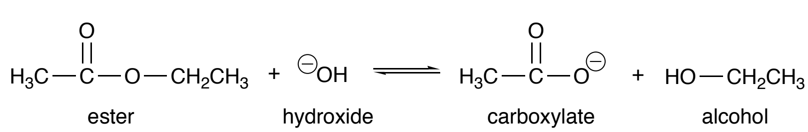
d. 

2. In nucleophilic acyl substitution, a nucleophile replaces a leaving group attached to a carbonyl, as in this general equation:

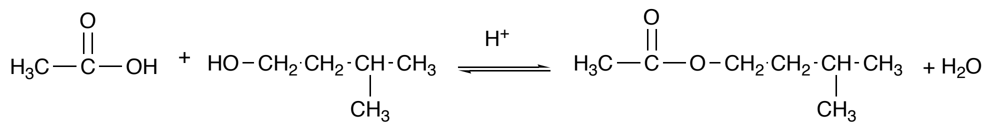


This reaction can be either acid- or base-catalyzed. Consider the base-catalyzed hydrolysis of an ester. The hydroxide ion (strong nucleophile) attacks the carbonyl carbon, and the carbonyl oxygen becomes an alkoxide. This is called a tetrahedral intermediate, as the carbonyl carbon is now sp^3 hybridized and tetrahedral in shape. Two electrons from the alkoxide oxygen re-form the C=O double bond, and the leaving group is kicked out. What is the better leaving group in the molecule? (remember, OH^- is an exceptionally poor leaving group). Finally after the leaving group is kicked out, it is usually a strong acid, so it will deprotonated the carboxylic acid proton, forming an alcohol and a carboxylate ion.

Without using your book, draw this mechanism for the base-catalyzed hydrolysis of the following carboxylic acid:



3. In an acid-catalyzed nucleophilic acyl substitution, there is no strong nucleophile present. One important example is the Fischer esterification, a reaction that combines a carboxylic acid and alcohol under acidic conditions to form an ester and water. This was how we made banana oil last semester:



acetic acid — isopentyl alcohol — isopentyl acetate — water

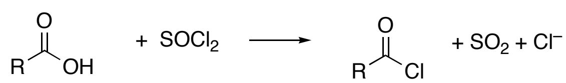
The Fischer esterification's mechanism can be broken into 2 parts:

a. **Acid-catalyzed addition of the alcohol to the carbonyl:** First, the carbonyl oxygen is protonated by acid. The carbonyl carbon is then sufficiently electrophilic to be attacked by the alcohol oxygen. We now have a tetrahedral intermediate (the former carbonyl carbon now has 4 bonds). The former alcohol oxygen is then deprotonated to make a neutral ester hydrate molecule.

b. Acid-catalyzed dehydration: One of the hydroxyl groups is protonated by acid and leaves, forming a resonance-stabilized carbocation. In the resonance structure with a C=O double bond, water will deprotonate the positively charged oxygen to make a neutral ester.

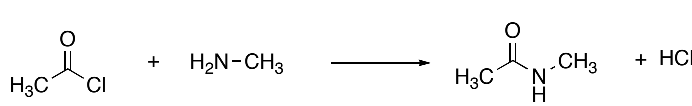
Without using your book, write this mechanism for the formation of isopentyl acetate (banana oil) in the reaction shown above.

4. Acid chlorides can be synthesized from any carboxylic acid through the use of thionyl chloride, $SOCl_2$:



carboxylic acid — thionyl chloride — acid chloride

An acid chloride can then be attacked by any nucleophile (strong or weak) to form an acid derivative (an ester, amide, or anhydride) through the loss of the chloride leaving group. First, the nucleophile attacks the carbonyl carbon, making a tetrahedral intermediate (the carbonyl carbon will now have 4 bonds). The electrons from the resulting alkoxide will re-form the C=O double bond, and the chloride ion will be kicked out. If the nucleophile was originally neutral, it will now have a + charge in the molecule, so it will be deprotonated by the chloride ion, forming HCl. Without using your book, draw the mechanism for the following reaction:



acid chloride — amine — amide