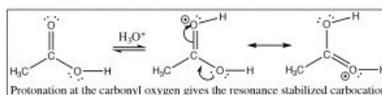


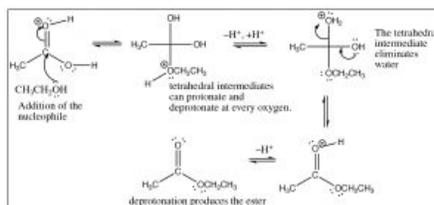
## 7.14: Nucleophilic Addition and Elimination Reactions of Acids and Derivatives

Just as with aldehydes and ketones, the reaction of acids and derivatives with oxygen and nitrogen nucleophiles is somewhat more complex: at each step, there is the potential for reversal. The formation and decomposition of the tetrahedral intermediate again plays a central role in the outcome of the reaction, and it is possible to use the knowledge of structure and properties to predict how the reaction will proceed. Furthermore, with a knowledge of how concentrations of reactants and products affect equilibrium positions, we can control the outcome of reactions using Le Chatelier's Principle.

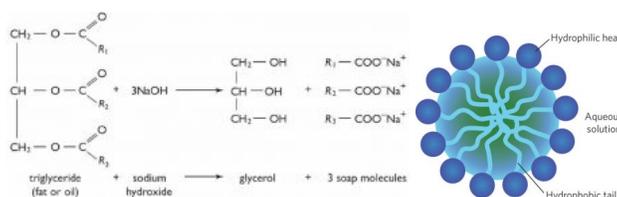


First, we will consider the reaction of a carboxylic acid with an alcohol leading to the formation of an ester. The reaction is typically performed with an acid catalyst and given that information, you should be able to write the mechanism. The first step is protonation; while there are two potentially basic oxygens, protonation tends to occur preferentially on the carbonyl oxygen (not the OH) because the resulting cation can be resonance-stabilized. As with aldehydes and ketones, protonation activates the carbonyl and the next step is attack by the nucleophile—in this case an alcohol. In the reaction scheme below, ethanol reacts with acetic acid to give ethyl acetate.

The crucial part of this mechanism is the series of tetrahedral intermediates that are interconverted by protonating and deprotonating the three different oxygens. Since all these groups are similar (OH or OR) the probability of each of these groups leaving is more or less the same once they are protonated. Just as with aldehydes and ketones, the system will become more stable (with stronger bonds) if the carbonyl group reforms by the elimination of one of the groups attached to the carbon. Again, we can shift the equilibrium for this reaction by manipulating the reaction conditions. Typically, esterifications are carried out using the alcohol as solvent (so it is in large excess), and the water produced is removed as it is formed.



As you might expect, this reaction is entirely reversible, and the reverse reaction is typically carried out in aqueous solution with either acid or base catalysis. In fact, this reaction is the basis of saponification (soap making); in which long-chained fatty acid esters of glycerol (triglycerides) are hydrolyzed in an aqueous solution with a base catalyst.



The triglyceride (fat or oil) is insoluble in water, while the sodium salt of the long-chain fatty acid (soap) is soluble. The soap molecules aggregate to form spherical micelles in which the polar head groups lie on the outside and the non-polar tails are inside<sup>[9]</sup>.

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