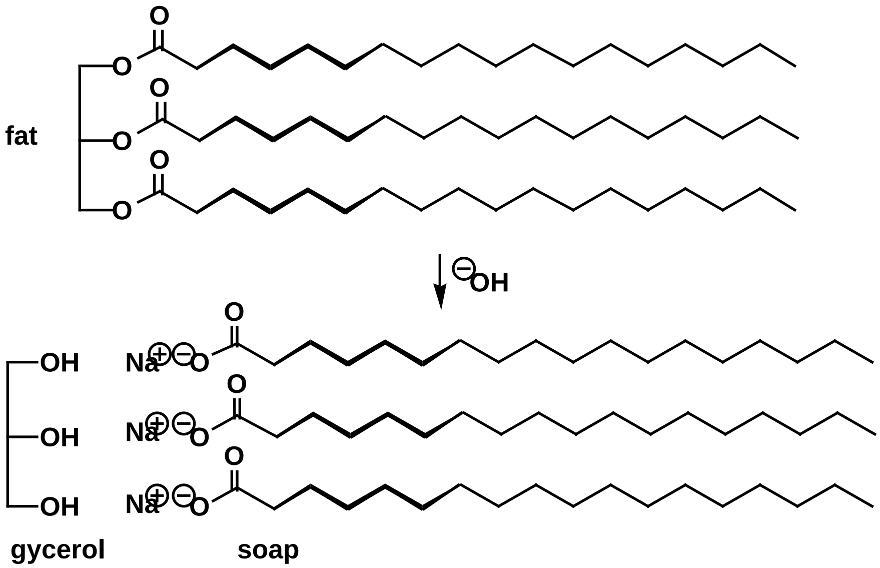
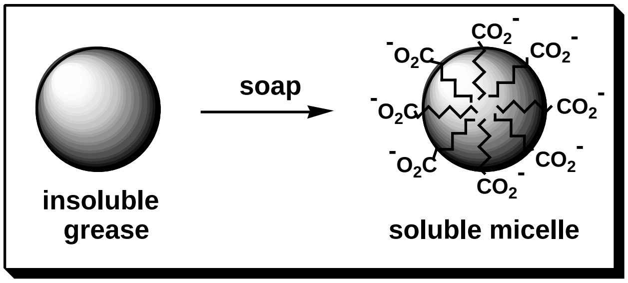
Text Related to Segments 19.02 & 19.03

This text covers the material of Segments 19.02 and 19.03 in a sequence to some extent the reverse of that in the corresponding video segments, to provide a second perspective on what often is a difficult set of concepts to keep straight when first introduced — regardless of order. However, as we elaborate on some details concerning the reactions of esters, it never should be forgotten that esters are, from the point of view of stoichiometry, simply the dehydration products resulting from combination of a carboxylic acid with an alcohol.

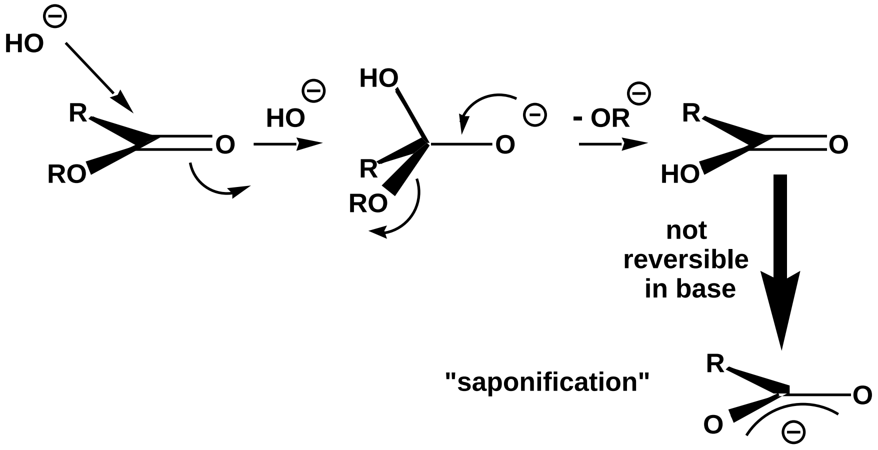
In one of the oldest known chemical reactions, doubtless stretching back to prehistory, it was discovered how to make a cleansing agent — soap — by heating animal fat with aqueous base, perhaps an adventitious solution of wood ashes. The transformation accomplished was the ester hydrolysis of the long-chain carboxylic acid esters of the triol glycerol (1,2,3-trihydroxypropane) which comprise animal fat. Commonly known as "saponification," the base-catalyzed hydrolysis of esters occurs by the substitution mechanism shown in the following figure. The reaction is irreversible, since it is driven to the right by the formation of the stable carboxylate anion, consuming in the process a full equivalent of base for each equivalent of carboxylic acid, and thus allowing the formally forbidden displacement of a stronger base (the alkylate anion, which, it should be noted, simultaneously can be, and is, protonated by water in the aqueous base solution) by a somewhat weaker base (hydroxide anion):



a supplementary comment:

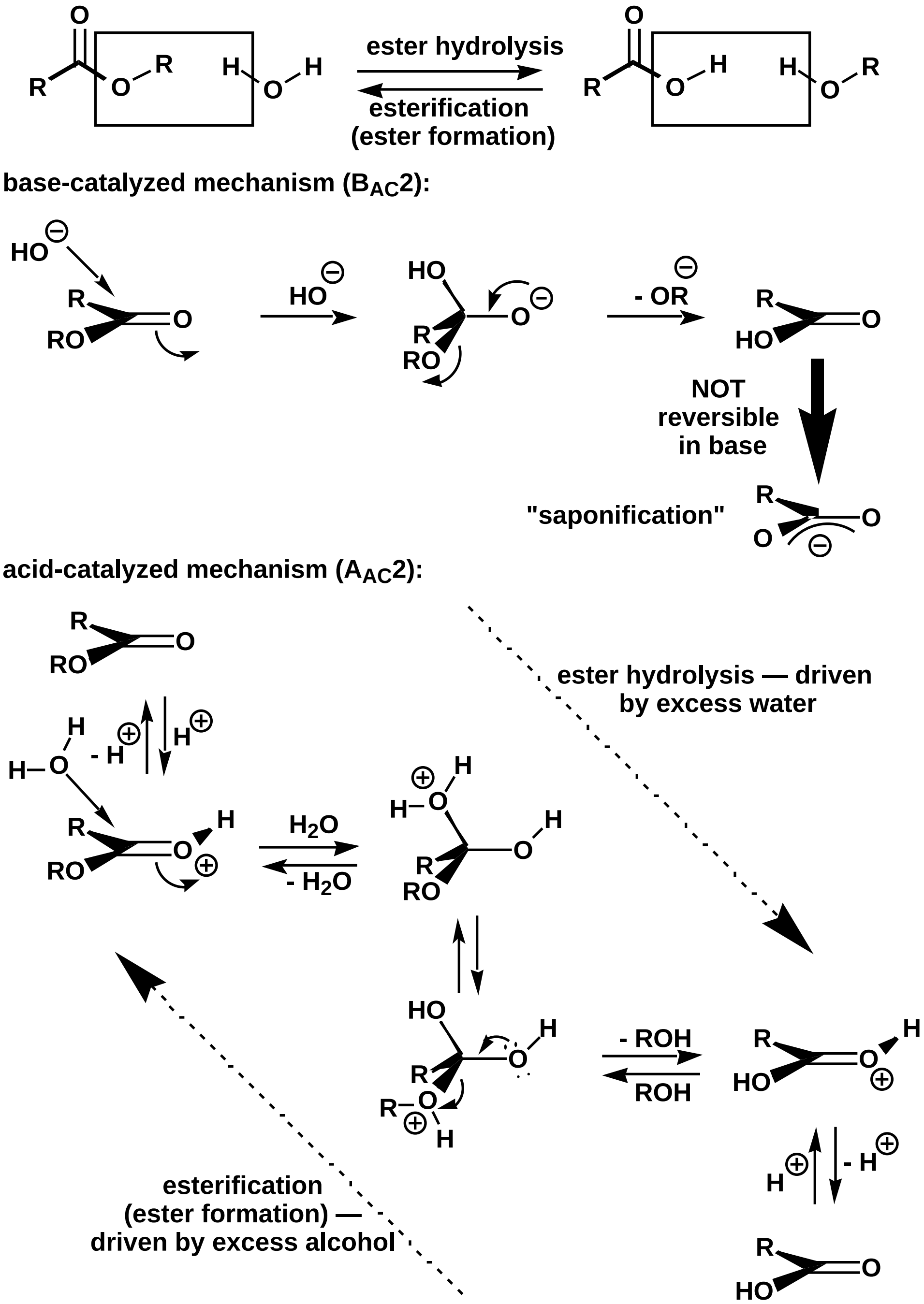


mechanism:



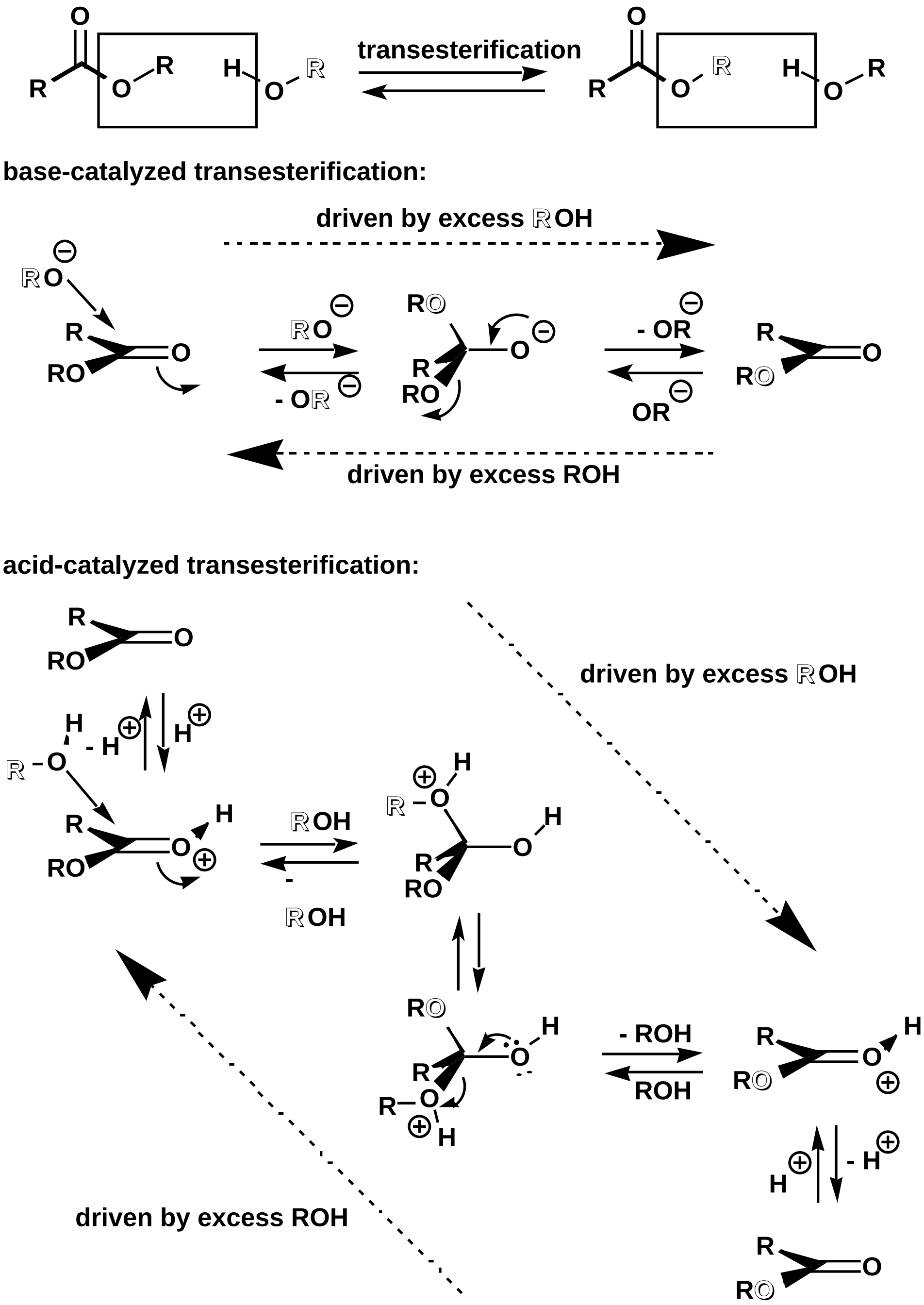
saponification (base-catalyzed hydrolysis) of esters

Acid-catalyzed hydrolysis of esters (next figure) follows a parallel route, the difference being that nucleophilic attack is carried out by the weak base water, rather than the strong base hydroxide ion; but on the *protonated* ester, which has enhanced electrophilicity, rather than on the free ester. The figure is arranged to emphasize this parallelism (notice the graphical identity of the "arrow-pushing" formalisms along the horizontal axes of the figure). It needs to be added that there exist other mechanisms of ester hydrolysis; the ones outlined (known as $B_{AC}2$ and $A_{AC}2$) are most commonly observed. Acid-catalyzed ester hydrolysis is driven by the excess of water present in the solution, the alcohol being, so to speak, lost in this solution. On the other hand, all one must do to reverse this acid-catalyzed situation is to increase the alcohol concentration. Thus, via precisely the same mechanism, except in the reverse sense, a carboxylic acid and an alcohol may be made to form an ester (esterification) by placing them together in the presence of an acid catalyst and, if necessary, removing water by physical or chemical means. Here is Le Chatelier's principle at work in one of its nicest manifestations! We should emphasize once again that esterification *cannot* be carried out in base, because in base the carboxylic acid is trapped as the too-stable carboxylate anion.



$A_{AC}2$ mechanism of reversible acid-catalyzed hydrolysis and formation of esters, contrasted with irreversible base-catalyzed ester hydrolysis ("saponification") from previous figure

Closely related transformations are base- and acid-catalyzed *transesterification,* in which the alcohol functionality of one ester is traded for another:



base- and acid-catalyzed transesterification

Again, transesterification is driven by factors of concentration: the alcohol in excess will determine the product. Note here that base- as well as acid-catalyzed transformations can be operative, since throughout the entire course of the reaction the free carboxylic acid never is formed; as a result, there is no chance of falling into the carboxylate anion energy well.