Carboxylic acid

Lecture-2

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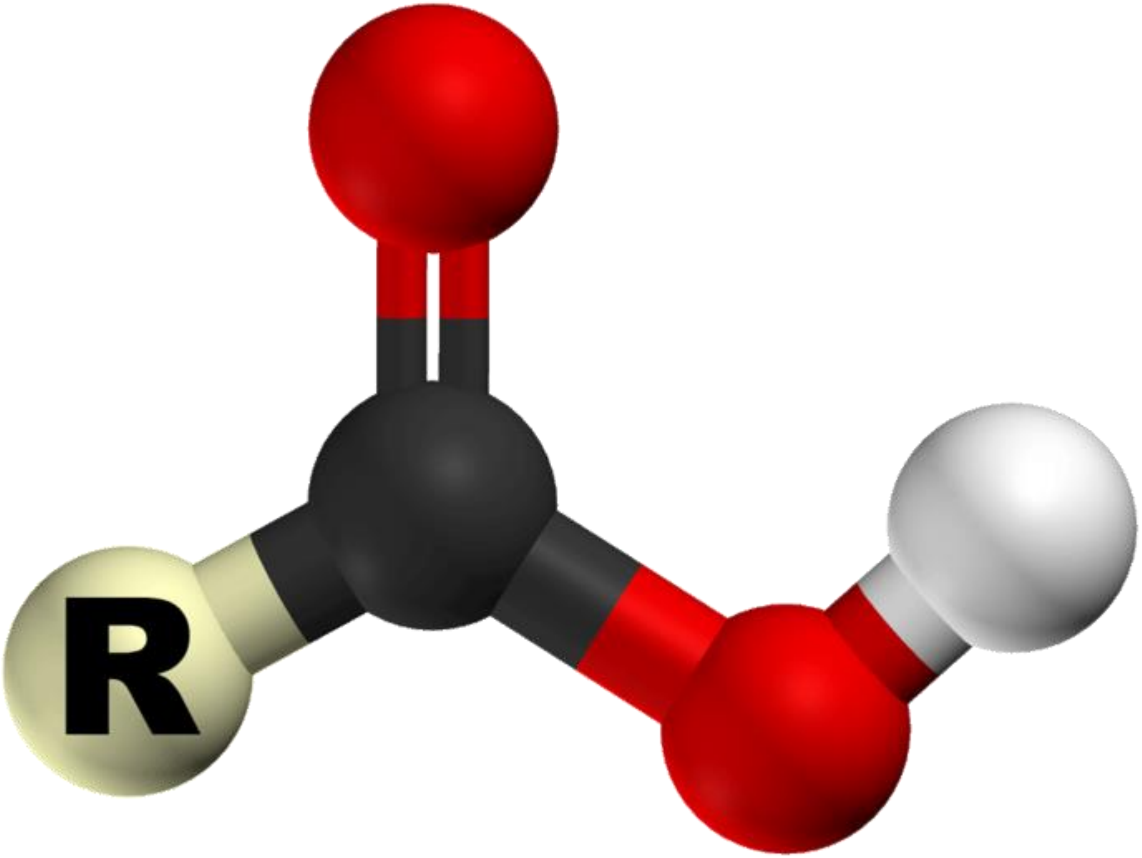
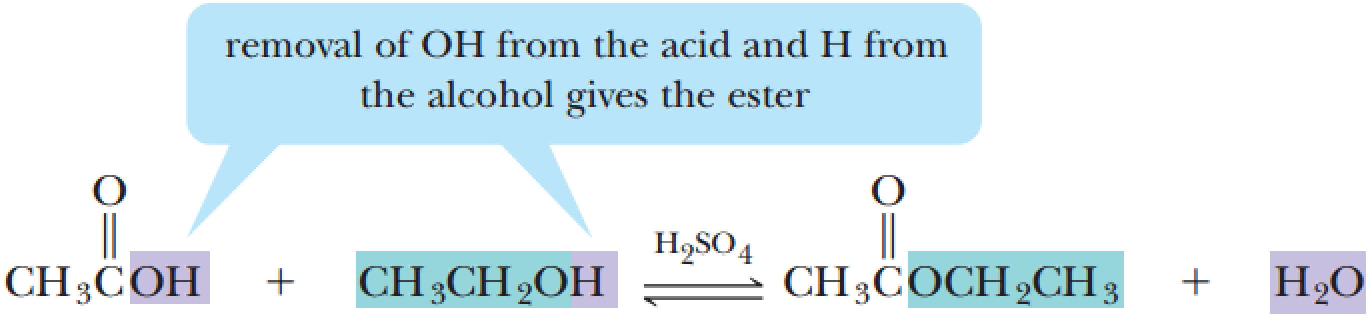
Carboxylic Acid



What Is Fischer Esterification?

Treatment of a carboxylic acid with an alcohol in the presence of an acid catalyst—most commonly, concentrated sulfuric acid—gives an ester. This method of forming an ester is given the special name **Fischer esterification** after the German chemist Emil Fischer (1852–1919). As an example of Fischer esterification, treating acetic acid with ethanol in the presence of concentrated sulfuric acid gives ethyl acetate and water:



removal of OH from the acid and H from the alcohol gives the ester

$$CH_3\overset{O}{\overset{\|}{C}}OH + CH_3CH_2OH \underset{}{\overset{H_2SO_4}{\rightleftharpoons}} CH_3\overset{O}{\overset{\|}{C}}OCH_2CH_3 + H_2O$$

Ethanoic acid (Acetic acid)

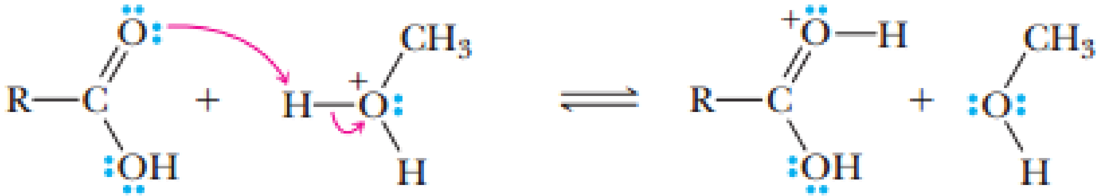
Ethanol (Ethyl alcohol)

Ethyl ethanoate (Ethyl acetate)

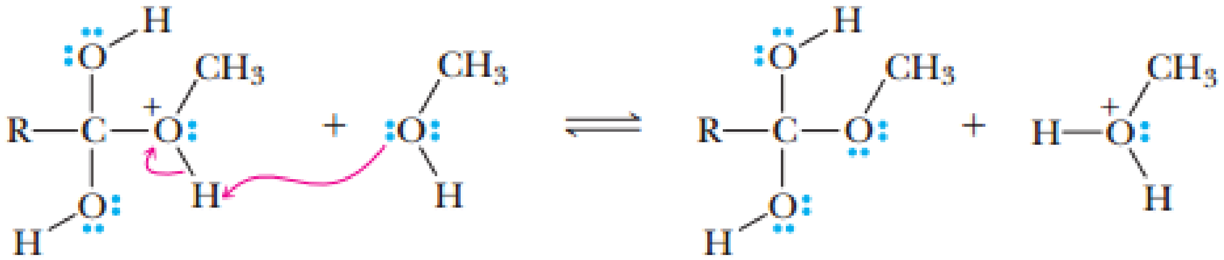
Acid-catalyzed esterification is reversible, and generally, at equilibrium, the quantities of remaining carboxylic acid and alcohol are appreciable. By controlling the experimental conditions, however, we can use Fischer esterification to prepare esters in high yields. If the alcohol is inexpensive compared with the carboxylic acid, we can use a large excess of the alcohol to drive the equilibrium to the right and achieve a high conversion of carboxylic acid to its ester.

Fischer Esterification Mechanism

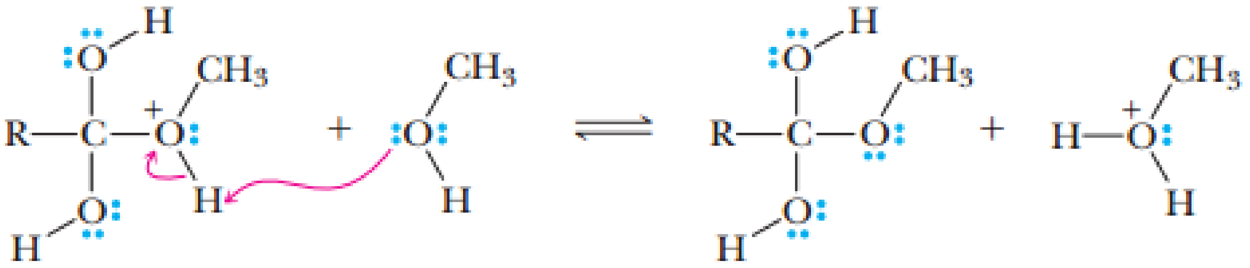
STEP 1: Add a proton. Proton transfer from the acid catalyst to the carbonyl oxygen increases the electrophilicity of the carbonyl carbon:



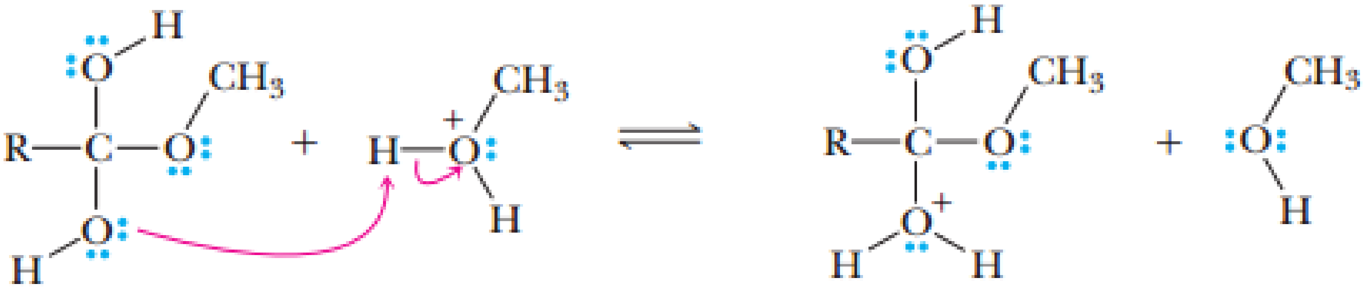
STEP 2: Reaction of a nucleophile and an electrophile to form a new covalent bond. The carbonyl carbon is then attacked by the nucleophilic oxygen atom of the alcohol to form an oxonium ion:



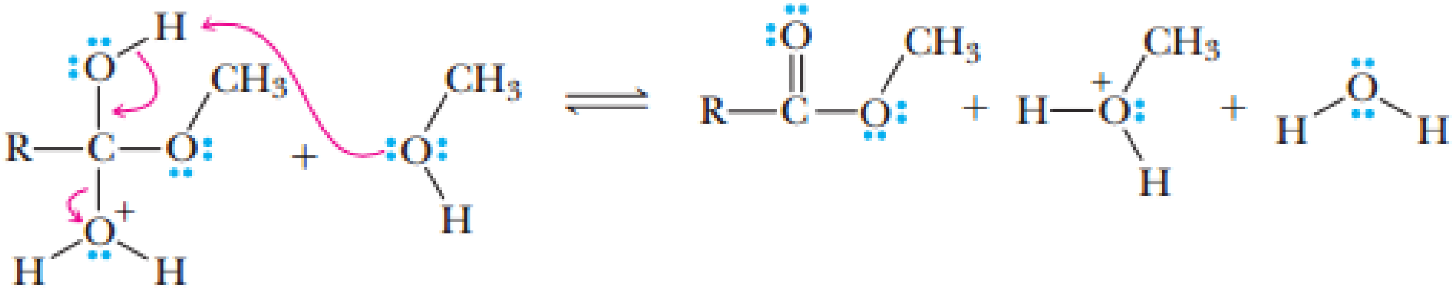
STEP 3: Take a proton away. Proton transfer from the oxonium ion to a second molecule of alcohol gives a tetrahedral carbonyl addition intermediate (TCAI):



STEP 4: Add a proton. Proton transfer to one of the J OH groups of the TCAI gives a new oxonium ion:



STEP 5: Collapse of the tetrahedral carbonyl addition intermediate to eject a leaving group and regenerate the carbonyl group. Loss of water from this oxonium ion gives the ester and regenerates the acid catalyst:



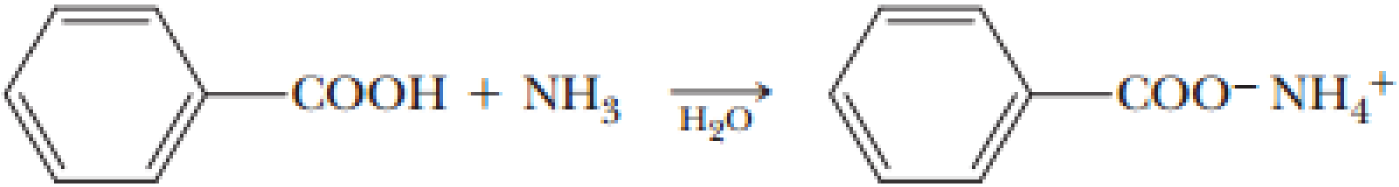
Reaction with Bases

All carboxylic acids, whether soluble or insoluble in water, react with NaOH, KOH, and other strong bases to form water-soluble salts:

Benzoic acid
(slightly soluble in water)

Sodium benzoate
(60 g/100 mL water)

Sodium benzoate, a fungal growth inhibitor, is often added to baked goods “to retard spoilage.”
Calcium propanoate is used for the same purpose.
Carboxylic acids also form water-soluble salts with ammonia and amines:

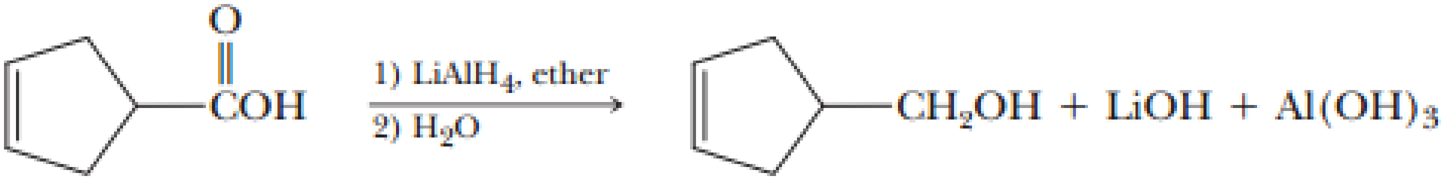


Benzoic acid
(slightly soluble in water)

Ammonium benzoate
(20 g/100 mL water)

Reduction of a Carboxyl Group

Lithium aluminum hydride, LiAlH4, reduces a carboxyl group to a primary alcohol in excellent yield. Reduction is most commonly carried out in diethyl ether or tetrahydrofuran (THF). The initial product is an aluminum alkoxide, which is then treated with water to give the primary alcohol and lithium and aluminum hydroxides:



3-Cyclopentene-carboxylic acid

4-Hydroxymethyl-cyclopentene

These hydroxides are insoluble in diethyl ether or THF and are removed by filtration.

Evaporation of the solvent yields the primary alcohol.

Alkenes are generally not affected by metal hydride-reducing reagents. These reagents function as hydride ion donors; that is, they function as nucleophiles, and alkenes are not normally attacked by nucleophiles.