

I. DEFINITION AND NOMENCLATURE OF CARBOXYLIC ACIDS (20.1)

- A. DEFINITION: A carboxylic acid contains a C=O whose C atom is bonded to an -OH group and another C atom.
- B. NOMENCLATURE: Nomenclature of carboxylic acids is divided into two groups: acyclic and cyclic carboxylic acids.
1. Acyclic carboxylic acids are named using the following rules.
 - a. The parent name is derived from the corresponding alkane based on the number of carbon atoms in the chain including the carbon atom of the carboxylic acid.
 - b. The "e" ending of the alkane is replaced with "oic acid".
 - c. The carbon atom of the acid is the #1 carbon atom when numbering the chain.
 2. Cyclic carboxylic acids are named using the following rules.
 - a. The parent name is derived from the corresponding cyclic alkane based on the number of carbon atoms in the ring.
 - b. When numbering the ring, the carbon atom which bears the carboxylic acid substituent is the number one atom.
 - c. The suffix used is "carboxylic acid". The "e" ending of the alkane parent is retained.
 3. There are a number of common names for carboxylic acids.
- C. CARBOXYLIC ACID DERIVATIVES
Carboxylic acid derivatives are carbonyl-containing functional groups where the carbonyl carbon is bonded to an electronegative element. These functional groups include esters, amides, acid chlorides and anhydrides. Nitriles are also considered to be carboxylic acid derivatives.

II. DEFINITION AND NOMENCLATURE OF NITRILES (20.1)

- A. Nitriles are organic functional groups that contain a C≡N (triple) bond.
- B. Nitriles are named as derivatives of carboxylic acids by replacing the "-ic acid" or "-oic acid" suffix with "-onitrile".
- C. The nitrile group may also be referred to as a "cyano-" group.

III. STRUCTURAL FEATURES OF CARBOXYLIC ACIDS (20.2)

- A. HYDROGEN BONDING
1. Carboxylic acids are capable of forming hydrogen bonds
 2. Carboxylic acids generally exist as dimeric species held together by H-bonds.
 3. The b.p. of carboxylic acids is generally higher than the b.p. of their corresponding alcohol or alkane derivatives.
- B. ACIDITY: Carboxylic acids are acidic compounds. (20.3-20.4)
1. pKa
 - a. The pKa of carboxylic acids is generally on the order of 4-6.
 2. SOLUBILITY
 - a. Carboxylic acids are soluble in base.
 - b. Carboxylic acids are generally soluble in H₂O if they contain fewer than 6 C atoms.
 - c. Carboxylate salts are soluble in water.
 - d. Calculating the percent ionization of a carboxylic acid
 3. EFFECTS OF SUBSTITUENTS ON pKa: Substituent effects of carboxylic acids, in general, and in particular in benzoic acids can affect the strength of an acid.
 - a. CARBOXYLIC ACIDS (GENERAL)
 - i. The more stable the carboxylate anion, the stronger the acid.
 - ii. Carboxylate anions are stabilized via an electron withdrawing group substituent via an "inductive effect".
 - iii. The further away the EWG, the less effect it has on the pKa of the acid.
 - iv. Electron donating groups destabilized the carboxylate anion and thus result in a weaker acid (higher pKa).
 - b. BENZOIC ACIDS
 - i. EWG on the benzene ring of benzoic acid stabilize the carboxylate anion.
 - ii. EWG's on the benzene ring of benzoic acids result in a stronger acid (lower pKa).
 - iii. Electron donating groups on the benzene ring of the benzoic acid destabilize the carboxylate anion and thus result in a weaker acid (higher pKa).

III. PREPARATION OF CARBOXYLIC ACIDS (20.5)

- A. CARBOXYLATION OF GRIGNARD & ALKYL LITHIUM REAGENTS
1. The electrophilic carbon atom of carbon dioxide reacts with the nucleophilic carbon atom of either a Grignard or an alkyllithium reagent to give a carboxylic acid.
- B. HYDROLYSIS OF NITRILES
1. Nitriles can be hydrolyzed with either strong aqueous acid or base to give carboxylic acids.
- C. OXIDATION OF BENZYLIC CARBON ATOMS
1. Primary and secondary benzylic carbon atoms can be oxidized with KMnO₄ / H₂O or Na₂Cr₂O₇.
 2. Tertiary benzylic carbon atoms cannot be oxidized.

D. OXIDATION OF ALKENES

1. Alkenes which contain at least one vinylic hydrogen atom can be oxidized to a carboxylic acid.
2. KMnO_4 (neutral or acidic), $\text{Na}_2\text{Cr}_2\text{O}_4$ or O_3 can be used to oxidize alkenes to carboxylic acids.

E. OXIDATION OF ALDEHYDES & PRIMARY ALCOHOLS

1. Primary alcohols can be oxidized to carboxylic acids using Jones reagent.
2. Aldehydes can be oxidized to carboxylic acids using Jones reagent or Tollens' reagent.

IV. REACTIONS OF CARBOXYLIC ACIDS (20.6)

A. ACID CATALYZED ESTERIFICATION (Fisher Esterification)

B. REDUCTION OF CARBOXYLIC ACIDS

1. Carboxylic acids can be reduced to primary alcohols with either LiAlH_4 or borane.

C. DECARBOXYLATION OF CARBOXYLIC ACIDS

1. Decarboxylation refers to loss of CO_2 from the reaction.
2. Decarboxylation is most commonly encountered with 1,3-dicarboxylic acids or their derivatives. This reaction is usually carried out with heat.
2. Decarboxylation of a carboxylic acid can be carried out in two ways.
 - i. Treatment of a carboxylic acid with HgO and X_2 provides an alkyl halide and CO_2 .
 - ii. Treatment of a carboxylic acid with Pb(IV) and X_2 provides an alkyl halide and CO_2 .