

Aliphatic Carboxylic Acids

Formulae
C_nH_{2n}O₂

- Ascending order of boiling points
- 1) HCOOH - Methanoic acid
 - 2) $\text{HOOCCH}_2\text{COOH}$ - Ethanoic acid
 - 3) CH_3COOH - Propanoic acid
 - 4) $\text{HO}_2\text{C}-\text{CH}_2-\text{CO}_2\text{H}$ - Butanedioic acid
 - 5) $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$ - Pentanoic acid
 - 6) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ - Hexanoic acid

2) Discusses briefly the physical properties of carboxylic acids under the following heading.

Physical appearance

All simple aliphatic carboxylic acids up to C₁₀ are liquids at room temperature. Most others are solid at room temperature although aliphatic carboxylic acids (glacial ethanoic acid) freeze to an ice-like solid below room temperature.

Boiling point

Boiling point increases with increasing relative molecular mass. Aromatic carboxylic acids are crystalline solids and have higher m.p. than their aliphatic counterparts of comparable relative molecular mass.

Solubility

Lower molecular mass carboxylic acids with up to four carbon atoms in their molecules are soluble in water, due to ability to form hydrogen bonds with water molecules. Water solubility of acids decreases as the R.M.M. increases. All carboxylic acids are soluble in organic solvents.

Write two industrial preparations of carboxylic acids

- 1) From carbon dioxide
Methanoic acid (formic acid) is manufactured by adding carbon dioxide under pressure to hot aqueous solution of sodium hydroxide. The free carboxylic acid is liberated by treating with H₂SO₄.
 $\text{CO}_2 + \text{NaOH} \rightarrow \text{HCOONa} + \text{NaOH} \rightarrow \text{HCOOH} + \text{NaOH}$

1) From ethanol

Ethanoic acid is obtained commercially by the liquid phase air-oxidation of 5% solution of ethanol to ethanoic acid with manganese(II) ethanoate catalyst. Ethanol itself is obtained from ethylene.
 $\text{HC} \equiv \text{CH} \xrightarrow{\text{O}_2, \text{H}_2\text{SO}_4/\text{Hg}^{2+}} \text{CH}_3\text{CHO} \xrightarrow{\text{O}_2/\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2} \text{CH}_3\text{COOH}$

4. With equations and brief explanation discuss the synthetic preparation of carboxylic acid.

1) Oxidation of primary alcohols and aldehydes
It can be used to prepare carboxylic acids using the usual oxidizing agents i.e. $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$, KMnO_4 in acidic solution.
 $\text{RCH}_2\text{OH} \xrightarrow{\text{KMnO}_4} \text{RCHO} \xrightarrow{[\text{O}]} \text{RCOOH}$

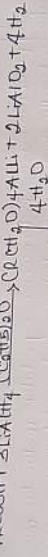
ii) Oxidation of Bergard reagent

Aliphatic carboxylic acid are obtained by bubbling carbon(IV) oxide into the reagent and then hydrolyzed with dilute acid.
 $\text{R MgBr} + \text{CO}_2 \xrightarrow{\text{C}_6\text{H}_5\text{MgBr}} \text{RCOOMgBr} \xrightarrow{\text{H}_2\text{O}/\text{dil. acid}} \text{RCOOH} + \text{MgBrOH}$

iii) Hydrolysis of nitriles (cyanides) or esters
 $\text{C}_2\text{H}_5\text{CO}_2\text{NH}_2 + 2\text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{C}_2\text{H}_5\text{CO}_2\text{OH} + \text{NH}_4^+$

5) With chemical equation only, outline the reduction, decarboxylation and iodination of carboxylic acid.

i) Reduction to primary alcohol



4H₂O



ii) Decarboxylation



iii) Esterification

