17. Carboxylic Acids & Derivatives

- Carboxylic acid molecules dimerise in the vapour state and in non-polar solvents
- *__Benzoic acid__ dissolves readily in hot water but forms white crystalline powder when cooled as it is only slightly soluble in cold water (due to large hydrophobic ring).
- Carboxylic acids are generally stable to oxidation except for **methanoic acid** and **ethanedioic acid**.
- Carboxylic acids are the most acidic organic compounds due to the high stability of the carboxylate ion (conjugate base) RCOO-
    - ➢ Delocalisation of the negative charge over 2 highly electronegative O atoms (resonance effect) results in the carboxylate anion being greatly stabilised and hence its formation is energetically favoured.
    - ➢ **Key-word: Resonance-stabilised carboxylate ion**
    - ➢ Note that the C-O bonds in the resonance-stabilised carboxylate ion are equal in length, i.e, the negative charge is equally distributed between the two oxygen atoms.
- **Acyl chlorides** are the most reactive of carboxylic acids derivatives, **hydrolysed** on contact with water
- Formation of esters from the reaction of an acyl chloride and a phenol requires an **alkaline medium** to first convert the phenol to a more nucleophilic phenoxide ion.
- In **esterification**, the reaction is reversible and the **equilibrium constant** is not very large, thus conc. H2SO4 is used as a catalyst to enhance nucleophilic attack on carbonyl carbon and remove water (shift eqm position to the right)
- *The eqm position is further driven to the right by using an excess of one of the reactants
- **Esterification and hydrolysis of esters is a reversible reaction as the stability of the products is similar.**
- Hydrolysis of esters is speeded by boiling/heating under reflux with acid or alkali.
- Using HCl(aq), the reaction is reversible and carboxylic acid is produced
- **However, using NaOH(aq), the carboxylate salt is produced instead and since the carboxylate salt is resonance stabilised, shows little tendency to react with an alcohol and thus the reaction is irreversible.** This reaction is called **saponification.**