4.5 Carboxylic acids and their derivatives

Relative acidity

Carboxylic acids are weak acids. The negative charge of the carboxylate ion is delocalised, which stabilises the ion allowing H^+ to exist.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

Phenols are weak acids. The negative charge of the phenoxide ion is delocalised, stabilising the ion.

Phenols are weaker acids than carboxylic acids because the delocalisation of the negative charge is less in the phenoxide ion than the carboxylate ion. This makes the phenoxide ion a weaker base than the carboxylate ion.

$$C_6H_5OH \rightleftharpoons C_6H_5O^- + H^+$$

Ethanol is a weaker acid than water. In the ethoxide ion, the negative charge is increased due to the electron donating effect of the alkyl group. The ethoxide ion is a stronger base than the hydroxide ion as hydrogen does not have the electron donating effect.

$$C_2H_5OH \rightleftharpoons C_2H_5O^- + H^+$$

$$H_2O \rightleftharpoons HO^- + H^+$$

Reduction

The reducing agent is lithium tetrahydridoaluminate(III), $LiAlH_4$ in ether. Carboxylic acids **are not** reduced by sodium tetrahydridoborate(III), $NaBH_4$.

$$R\text{-}COOH \xrightarrow{LiAlH_4} RCH_2OH$$

$$R\text{-}COOH + 4[H] \rightarrow RCH_2OH + H_2O$$

Decarboxylation

If a carboxylic acid or its sodium salt is strongly heated with soda lime, the carboxylate group, COO^-, is removed.

$$CH_3CH_2COOH + 2NaOH \rightarrow C_2H_6 + Na_2CO_3$$

$$CH_3CH_2COONa + NaOH \rightarrow C_2H_6 + Na_2CO_3$$

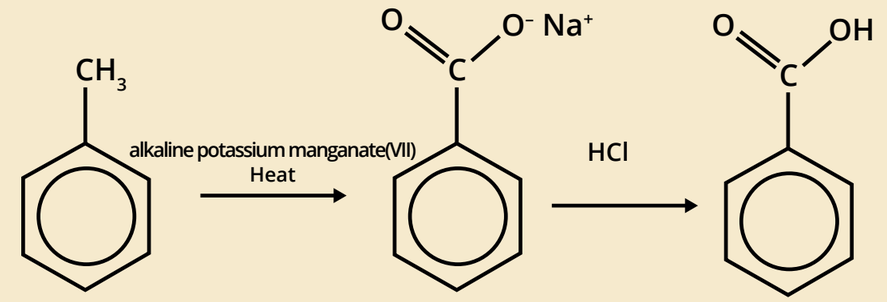
Formation

Carboxylic acids are formed from primary alcohols and aldehydes by oxidation with acidified dichromate, $Cr_2O_7^{2-}/H^+$.

$$CH_3CH_2CH_2OH \rightarrow CH_3CH_2COOH$$

$$CH_3CH_2CHO \rightarrow CH_3CH_2COOH$$

Aromatic carboxylic acids are formed by the oxidation of a side chain of an aromatic compound by heating with alkaline potassium manganate(VII). The product is a salt of the acid since the conditions are alkaline and the mixture must be acidified with hydrochloric acid to release the free acid.



methylbenzene — sodium benzenecarboxylate — benzenecarboxylic acid

Derivatives

Esters

Prepared by heating a carboxylic acid and an alcohol with a strong acid catalyst, usually concentrated H_2SO_4.

$$RCOOH + R_1OH \rightarrow RCOOR_1 + H_2O$$

$$CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5 + H_2O$$

ethanoic acid ethanol ethyl ethanoate

Acid chlorides

Prepared by the reaction between a carboxylic acid and phosphorus pentachloride, PCl_5. Dry conditions are required.

$$CH_3OOOH + PCl_5\ CH_3OOCl \rightarrow + POCl_3 + HCl$$

ethanoyl chloride

Amides

Prepared by the reaction between a carboxylic acid and ammonium carbonate or ammonia. The mixture is heated under reflux. The ammonium salt dehydrates on heating.

$$(NH_4)_2CO_3 + RCOOH \rightarrow RCOO^-NH_4^+ + CO_2 + H_2O$$

$$NH_3 + RCOOH \rightarrow RCOO^-NH_4^+$$

$$RCOO^-NH_4^+ \rightarrow RCONH_2 + H_2O$$

If the amide is then heated with phosphorus(V) oxide, P_4O_{10}, a dehydration reaction occurs to produce a nitrile.

$$RCONH_2 \rightarrow RCN + H_2O$$

Hydrolysis reactions

Esters are not readily hydrolysed by water but are in the presence of a dilute acid or alkali.

Acid hydrolysis

$$RCOOR_1 + H_2O \rightarrow RCOOH + R_1OH$$

Alkaline hydrolysis

$$RCOOR_1 + NaOH \rightarrow RCOO^-Na^+ + R_1OH$$

To produce the carboxylic acid in alkaline hydrolysis, a dilute acid is added to hydrolyse the salt that was formed.

$$RCOO^- + H^+ \rightarrow RCOOH$$

Acid chlorides are readily hydrolysed by water.

$$RCOCl + H_2O \rightarrow RCOOH + HCl$$

Amides are not readily hydrolysed by water but are in the presence of a dilute acid or alkali.

Acid hydrolysis

$$RCONH_2 + H_2O + H^+ \rightarrow RCOOH + NH_4^+$$

Alkaline hydrolysis

$$RCONH_2 + NaOH \rightarrow RCOO^-Na^+ + NH_3$$

Nitriles are not readily hydrolysed by water but are in the presence of a dilute acid or alkali.

Acid hydrolysis

$$RCN + 2H_2O + H^+ \rightarrow RCOOH + NH_4^+$$

Alkaline hydrolysis

$$RCN + NaOH \rightarrow RCOO^-Na^+ + NH_3$$