3.3.9 Carboxylic Acids and Derivatives

★ A-LEVEL ONLY — not examined at AS level

3.3.9.1 *Carboxylic acids and esters: esterification, hydrolysis (acid and alkaline). Biodiesel. Soap.*

Carboxylic acids are weak acids — strong enough to liberate CO2 from carbonates: 2RCOOH + Na2CO3 → 2RCOONa + H2O + CO2.

Esterification: RCOOH + R'OH ■ RCOOR' + H2O (conc. H2SO4 catalyst, reflux). Reversible, low yield.

Esters: fruity smells; used as solvents, plasticisers, perfumes, food flavourings.

Acid hydrolysis of esters: RCOOR' + H2O ■ RCOOH + R'OH (reversible, dilute acid, reflux).

Alkaline hydrolysis (saponification): RCOOR' + NaOH → RCOONa + R'OH (irreversible — carboxylate salt formed).

Soap: fats/oils (triglycerides) + NaOH → sodium salt of long-chain carboxylic acid (soap) + glycerol.

Biodiesel: methyl esters of long-chain fatty acids, made from vegetable oils + methanol + catalyst (transesterification).

3.3.9.2 *Acylation: acyl chlorides and acid anhydrides with water, alcohols, ammonia, amines. Mechanisms. Aspirin.*

Acyl chlorides (RCOCl) and acid anhydrides ((RCO)2O) react via nucleophilic addition–elimination:

+ Water → carboxylic acid + HCl (or carboxylic acid from anhydride).

+ Alcohol → ester + HCl (or carboxylic acid).

+ Ammonia → primary amide + HCl (or carboxylic acid).

+ Primary amine → N-substituted amide + HCl (or carboxylic acid).

Mechanism (acyl chlorides): nucleophile attacks δ+C of C=O. C=O π-bond breaks. Cl■ leaves (addition–elimination).

Aspirin manufacture: ethanoic anhydride preferred over ethanoyl chloride — cheaper, less corrosive, reacts less vigorously (safer), produces ethanoic acid (not HCl) as by-product.

★ RPR P10 **Preparation of a Pure Organic Solid — Aspirin**

Method: Weigh salicylic acid (2-hydroxybenzoic acid) into a flask. Add ethanoic anhydride + few drops conc. H3PO4 (catalyst). Heat in water bath at 80–90°C for 15 min. Cool; add cold distilled water to decompose excess anhydride. Cool in ice bath until crystals form; scratch flask to encourage crystallisation. Filter under reduced pressure (Buchner funnel). Wash with cold water. Recrystallise: dissolve in minimum hot ethanol, add warm water, cool slowly then in ice. Filter, wash, dry. Measure melting point (aspirin: 135°C) and compare with literature value.

Uncertainties: balance ±0.001 g; thermometer ±0.5°C; melting point apparatus ±1°C.

Common errors: not heating long enough (incomplete reaction); adding water too quickly (splattering); not cooling enough before filtering; impure product (broad melting point range).

Improvements: heat for full time; add water slowly to cooled mixture; cool in ice bath; recrystallise for purity; sharp m.p. close to literature = high purity.