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It's Important to Know!

BP202T — Pharmaceutical Organic Chemistry I

B.Pharm Semester 2 · Unit 5 — Carboxylic Acids and Aliphatic Amines

Unit V: Carboxylic Acids and Aliphatic Amines

Carboxylic acids

Carboxylic acids contain a carboxyl group and can donate a proton. Their acidity is influenced by resonance stabilisation of the conjugate base and by substituent effects. Electron-withdrawing groups usually increase acidity when they are positioned to influence the carboxyl group.

Carboxylic acids can form salts, esters and amides. Esterification is an equilibrium process between an acid and alcohol under suitable catalytic conditions. Amides are less basic than amines because the nitrogen lone pair is delocalised toward the carbonyl group.

The carboxylate conjugate base is stabilised because negative charge is shared across two oxygen atoms by resonance. An electron-withdrawing substituent can stabilise this anion through induction and increase acidity; an electron-donating substituent can have the opposite effect. The effect generally weakens with distance from the carboxyl group. These trends help compare acids, but solvent and molecular structure also influence measured acidity.

In esterification, the carbonyl oxygen is protonated under acid catalysis, increasing electrophilicity. The alcohol oxygen attacks the carbonyl carbon, proton transfers occur, water is eliminated, and deprotonation regenerates the catalyst. Because the reaction is reversible, removing water or using excess of one reactant can shift the equilibrium toward ester. The exact conditions depend on the substrates and safety requirements.

Aliphatic amines

Amines are derivatives of ammonia in which hydrogen atoms are replaced by carbon groups. Their basicity depends on electron donation, solvation, steric effects and resonance. Primary, secondary and tertiary amines differ in the number of carbon groups attached to nitrogen.

Qualitative amine tests use reactions such as salt formation or derivatisation.

Amines act as bases because the nitrogen lone pair can accept a proton. Alkyl groups can increase electron density by induction, but solvation and steric effects alter the observed basicity in water. Aromatic amines are generally less basic than comparable aliphatic amines because the lone pair can be delocalised into the aromatic system. Amides are still less basic because their nitrogen lone pair is strongly delocalised toward the carbonyl group.

Worked acidity and basicity comparisons

When comparing two carboxylic acids, first draw no structure but identify the substituent's electronic effect and its distance from the carboxyl group. An electron-withdrawing group close to the acid usually increases acidity by stabilising the conjugate base. When comparing amines, assess lone-pair availability, induction, resonance and solvation. In an amide, resonance with the carbonyl makes the nitrogen lone pair less available, so it is less basic than an amine. Numerical pKa comparisons require a specified solvent and reliable reference data.

Unit V: Frequently asked questions

Q: Why are electron-withdrawing groups important in carboxylic acid acidity?

A: They stabilise the negatively charged conjugate base through inductive effects and can increase acidity.

Q: Why are amides less basic than amines?

A: The amide nitrogen lone pair is delocalised toward the carbonyl group and is less available to accept a proton.

Q: What is esterification?

A: It is formation of an ester from a carboxylic acid and an alcohol under suitable conditions, usually with water as a by-product.

Unit V: Key takeaways

- Carboxylic acid acidity depends on conjugate-base stability and substituent effects.
- Acids form salts, esters and amides.
- Amines are basic because nitrogen can accept a proton.
- Amide resonance reduces nitrogen basicity.
- Specific compound uses and test observations require verified references.

Unit V: Practical correlation

Practical correlation: laboratory identification. Acid-base behaviour, solubility and a confirmatory derivative can be combined in an identification scheme.