FSc / ICS Part-II Chemistry — Punjab Board

CHAPTER 13
Carboxylic Acids

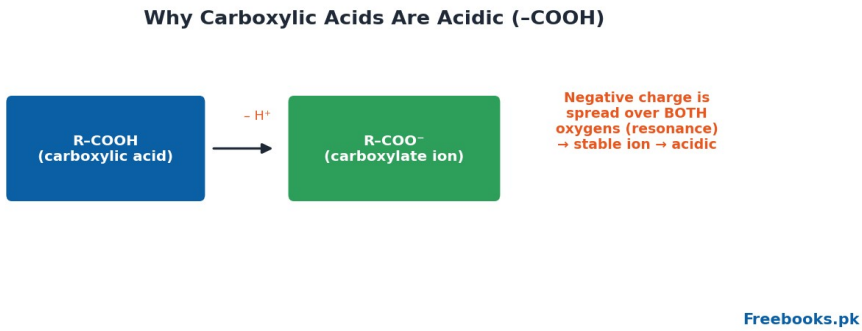

Figure 13.1 — Why carboxylic acids are acidic: the carboxylate ion is stabilised by resonance.

1. Chapter Overview

Carboxylic acids contain the carboxyl group (–COOH), which is really a combination of a carbonyl (C=O) and a hydroxyl (–OH) group on the same carbon. They are the most acidic of the common organic compounds, and are found everywhere in daily life — vinegar (ethanoic acid), citrus fruits (citric acid), sour milk (lactic acid) and ants (formic/methanoic acid). This chapter explains why carboxylic acids are acidic, how they are prepared, and their reactions, many of which produce important derivatives such as esters, acid chlorides and amides.

2. Learning Objectives

- Identify the carboxyl group and name simple carboxylic acids.
- Explain why carboxylic acids are acidic using resonance.
- Describe methods of preparing carboxylic acids.
- Describe the reactions of carboxylic acids and their derivatives.
- Explain esterification and its reverse, hydrolysis.
- State the important uses of carboxylic acids.

3. Key Concepts

3.1 The Carboxyl Group and Acidity

The carboxyl group –COOH is the functional group of carboxylic acids. These compounds are acidic because, when the O–H bond breaks and a proton is lost, the resulting carboxylate ion ($–COO^-$) is stabilised by resonance: the negative charge is shared equally between the two oxygen atoms, and the two C–O bonds become identical. This spreading of the charge makes the ion stable and the loss of the proton favourable, so carboxylic acids are far more acidic than alcohols or phenols (though still weak acids).

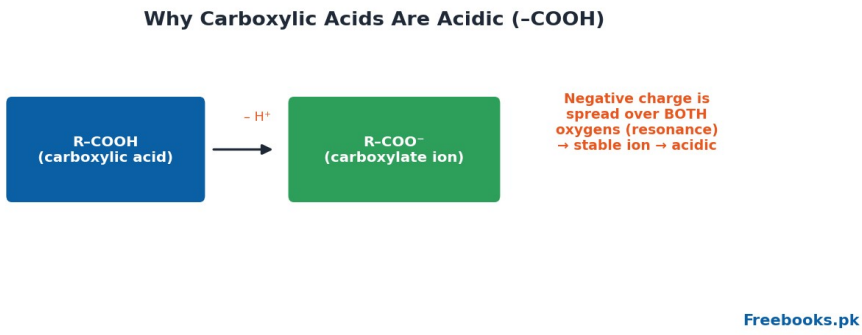

Figure 13.2 — Resonance stabilisation of the carboxylate ion.

> **Memory Trick**
> **Acidity order:** carboxylic acid > phenol > water > alcohol. 'Acids beat phenols beat alcohols.'

3.2 Preparation

Carboxylic acids can be prepared in several ways: by the oxidation of primary alcohols or aldehydes, by the hydrolysis of nitriles (R–CN + $2H_2O$ → R–COOH + NH_3), and by treating a Grignard reagent with carbon dioxide followed by hydrolysis (R–MgX + CO_2 → R–COOH), which adds one carbon to the chain. Ethanoic acid is made industrially from ethanol or ethene.

3.3 Reactions of Carboxylic Acids

The reactions of carboxylic acids fall into two groups: those of the acidic O–H, and those that replace the –OH of the carboxyl group to form derivatives.

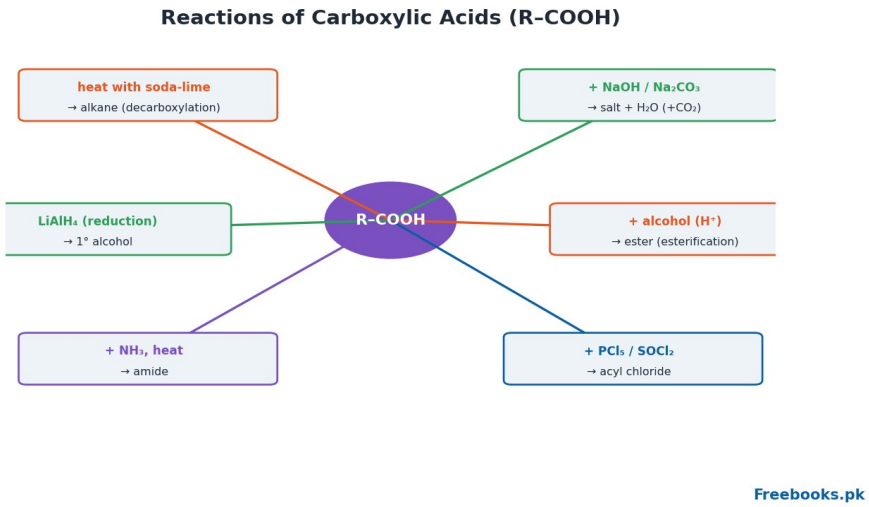

Figure 13.3 — Reactions of carboxylic acids and their derivatives.

Salt formation. As acids they react with metals, bases and carbonates to form salts; the reaction with sodium carbonate releases carbon dioxide (effervescence), a useful test.

Esterification. With an alcohol and a trace of acid catalyst they form a sweet-smelling ester and water; this reaction is reversible, and the reverse (with water) is hydrolysis.

Formation of acyl chlorides. With PCl_5, PCl_3 or $SOCl_2$ the –OH is replaced by –Cl to give a reactive acyl chloride.

Formation of amides. With ammonia (via the ammonium salt, on heating) they give amides (R–$CONH_2$).

Reduction. Strong reducing agents such as $LiAlH_4$ reduce carboxylic acids to primary alcohols.

Decarboxylation. On heating their sodium salts with soda-lime, carboxylic acids lose CO_2 to give an alkane with one fewer carbon.

> **Teacher's Note**
>
> Point out that all the 'derivative' reactions (ester, acyl chloride, amide) replace the –OH of –COOH with a different group. Seeing this pattern helps students remember the whole set.

3.4 Uses

Carboxylic acids and their derivatives are widely used: ethanoic acid (vinegar) as a food preservative and to make esters and other chemicals; methanoic acid in leather and rubber processing; benzoic acid and its salts as food preservatives; and long-chain fatty acids to make soaps. Esters of carboxylic acids are used as flavourings and perfumes.

4. Important Definitions

Term	Definition
Carboxylic acid	An organic compound containing the –COOH (carboxyl) group.
Carboxylate ion	The $–COO^-$ ion formed when a carboxylic acid loses a proton; stabilised by resonance.
Esterification	Reaction of a carboxylic acid with an alcohol to form an ester and water.
Hydrolysis	The breaking of a bond by water; the reverse of esterification.
Acyl chloride	A reactive derivative R–COCl formed by replacing –OH of –COOH with –Cl.
Decarboxylation	Loss of CO_2 from a carboxylic acid (or its salt) to give an alkane.

5. Formulas / Rules

Must-Know Facts

Functional group: –COOH (carbonyl + hydroxyl).

Acidic because the carboxylate ion is resonance-stabilised.

Acidity order: carboxylic acid > phenol > water > alcohol.

Test: with Na_2CO_3 gives CO_2 effervescence (distinguishes acids from phenols/alcohols).

Derivatives: ester (with alcohol), acyl chloride (PCl_5), amide (NH_3).

Grignard + CO_2 → carboxylic acid (adds one carbon).

6. Diagrams / Illustrations

Key diagrams for revision:

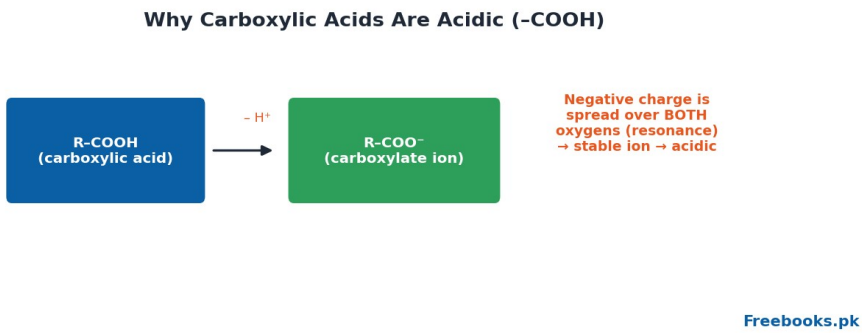

Diagram 1 — Acidity and resonance.

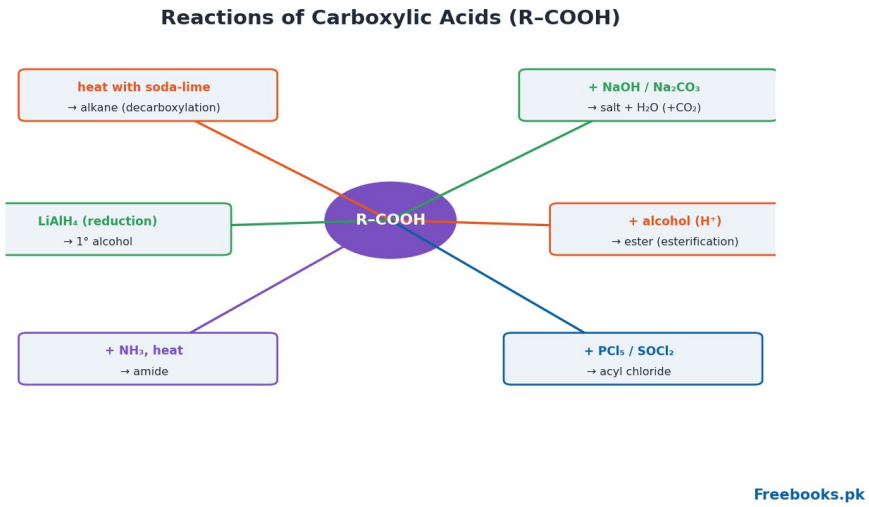

Diagram 2 — Reactions and derivatives.

7. Solved Examples

Example 1 — Why acidic

Q: Why is ethanoic acid more acidic than ethanol?

Solution: When ethanoic acid loses H^+, the carboxylate ion is stabilised by resonance (charge shared over two oxygens). Ethanol's alkoxide ion has no such stabilisation, so ethanoic acid is much more acidic.

Example 2 — Distinguishing test

Q: How can you distinguish a carboxylic acid from a phenol?

Solution: Add sodium carbonate (or sodium bicarbonate). A carboxylic acid gives brisk effervescence of CO_2; a phenol, being a weaker acid, does not react with sodium carbonate.

Example 3 — Esterification

Q: Write the product when ethanoic acid reacts with ethanol.

Solution: With a little concentrated H_2SO_4 they form the ester ethyl ethanoate (ethyl acetate) and water: $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$.

8. Short Questions

Q1. What is the functional group of carboxylic acids?
Ans. The carboxyl group, –COOH.

Q2. Why are carboxylic acids acidic?
Ans. Because the carboxylate ion left after losing H^+ is stabilised by resonance.

Q3. Arrange alcohol, phenol and carboxylic acid in order of acidity.
Ans. Carboxylic acid > phenol > alcohol.

Q4. How can a carboxylic acid be distinguished from a phenol?
Ans. A carboxylic acid gives CO_2 effervescence with sodium carbonate; a phenol does not.

Q5. What is esterification?
Ans. The reaction of a carboxylic acid with an alcohol to form an ester and water.

Q6. What is formed when a carboxylic acid reacts with PCl_5?
Ans. An acyl (acid) chloride, R–COCl.

Q7. What is decarboxylation?
Ans. Loss of CO_2 from a carboxylic acid (or its salt) to give an alkane, e.g. on heating with soda-lime.

Q8. How is a carboxylic acid made from a Grignard reagent?
Ans. By reacting R–MgX with CO_2 and then hydrolysing; this adds one carbon.

9. Long Questions

Q1. Explain why carboxylic acids are acidic.

Carboxylic acids are acidic because they readily give up the hydrogen of their –OH group as a proton, and the ion that is left behind is unusually stable. When a carboxylic acid loses H^+, it forms a carboxylate ion, $R–COO^-$. In this ion the negative charge is not fixed on one oxygen; instead it is delocalised by resonance so that both oxygen atoms share it equally, and the two carbon–oxygen bonds become identical in length. This spreading out of the charge lowers the energy of the ion and makes it stable, so the acid loses its proton easily. In contrast, when an alcohol loses a proton the resulting alkoxide ion has its charge fixed on a single oxygen with no resonance stabilisation, which is why alcohols are essentially neutral. Phenols lie in between, because their charge is delocalised into the ring but not as effectively. This is why the order of acidity is carboxylic acid > phenol > water > alcohol. Even so, carboxylic acids are still weak acids and only partly ionise in water.

Q2. Describe the important reactions of carboxylic acids.

Carboxylic acids react both as acids and by forming derivatives. As acids they turn blue litmus red and react with reactive metals, with bases and with carbonates to form salts; the reaction with sodium carbonate releases carbon dioxide, which is used as a test. The rest of their reactions replace the –OH of the carboxyl group with another group to give a derivative. With an alcohol and an acid catalyst they undergo esterification to form a sweet-smelling ester and water, a reversible reaction whose reverse is hydrolysis. With phosphorus pentachloride, phosphorus trichloride or thionyl chloride they form reactive acyl chlorides. With ammonia, through the ammonium salt on heating, they form amides. Strong reducing agents such as lithium aluminium hydride reduce them to primary alcohols. Finally, heating their sodium salts with soda-lime causes decarboxylation, removing carbon dioxide to leave an alkane with one fewer carbon. These reactions make carboxylic acids a gateway to many other organic compounds.

Q3. What is esterification? Discuss the reaction and its importance.

Esterification is the reaction in which a carboxylic acid combines with an alcohol, in the presence of a small amount of a strong acid catalyst such as concentrated sulphuric acid, to form an ester and water. For example, ethanoic acid and ethanol give ethyl ethanoate: $CH_3COOH + C_2H_5OH$

⇌ $CH_3COOC_2H_5$ + H_2O. The reaction is reversible, so it never goes fully to completion under ordinary conditions; the yield can be improved by using an excess of one reactant or by removing the water or ester as it forms. The reverse reaction, in which an ester is split by water back into an acid and an alcohol, is called hydrolysis (and when it is carried out with alkali it is called saponification, the basis of soap-making). Esterification is important because esters have pleasant, fruity smells and are widely used as artificial flavourings and perfumes, as solvents, and as the basis of fats, oils and many polymers.

10. Multiple Choice Questions (MCQs)

1. The functional group of carboxylic acids is:
(A) –OH (B) –CHO (C) –COOH (D) C=O

2. Carboxylic acids are acidic because the carboxylate ion is stabilised by:
(A) hydrogen bonding (B) resonance (C) ionic bonding (D) catenation

3. Which is the most acidic?
(A) ethanol (B) phenol (C) ethanoic acid (D) water

4. A carboxylic acid + Na_2CO_3 gives:
(A) H_2 (B) CO_2 (C) O_2 (D) NH_3

5. Acid + alcohol (H^+) gives:
(A) amide (B) ester (C) acyl chloride (D) alkane

6. Acid + PCl_5 gives:
(A) ester (B) amide (C) acyl chloride (D) alcohol

7. Reduction of a carboxylic acid ($LiAlH_4$) gives:
(A) aldehyde (B) 1° alcohol (C) ketone (D) ester

8. Grignard reagent + CO_2 (then H_2O) gives:
(A) alcohol (B) carboxylic acid (C) ketone (D) amide

9. Heating a sodium carboxylate with soda-lime gives:
(A) alkene (B) alkane (C) alcohol (D) ester

10. The reverse of esterification is:
(A) oxidation (B) hydrolysis (C) reduction (D) decarboxylation

MCQ Answer Key

1-C 2-B 3-C 4-B 5-B 6-C 7-B 8-B 9-B 10-B

11. Quick Revision / Summary

- –COOH group; acidic because carboxylate ion is resonance-stabilised.
- Acidity: carboxylic acid > phenol > water > alcohol.
- Preparation: oxidise 1° alcohol/aldehyde; hydrolyse nitrile; Grignard + CO_2.
- Reactions: salts (CO_2 with Na_2CO_3), esterification, acyl chloride (PCl_5), amide (NH_3), reduction, decarboxylation.
- Esterification is reversible; reverse = hydrolysis (with alkali = saponification).

- Uses: vinegar, preservatives, soaps, flavours/perfumes (esters).

12. Exam Tips

Teacher's Note

Explain acidity with the resonance of the carboxylate ion — a guaranteed question.
Na_2CO_3 effervescence distinguishes acids from phenols/alcohols — remember this test.
Learn the derivative reactions as 'replacing –OH': ester, acyl chloride, amide.
Esterification is reversible; know both directions and the catalyst (conc. H_2SO_4).
Grignard + CO_2 adds one carbon to give an acid — a common synthesis question.