▶ Video explanation (YouTube Short)

Why Carboxylic Acids Boil So High: Dimers

Carboxylic acids boil at higher temperatures than aldehydes, ketones and even alcohols of comparable molecular mass (NCERT 8.8).

1. The comparison (M ≈ 58–60 g/mol)

Compound	Family	M (g/mol)	b.p.
butane	alkane	58	≈ 0 °C (−1 °C)
propanal	aldehyde	58	49 °C
propan-1-ol	alcohol	60	97 °C
ethanoic (acetic) acid	carboxylic acid	60	118 °C

2. The reason: hydrogen-bonded dimers

The O–H hydrogen of one acid molecule bonds to the C=O oxygen of a second molecule, and the second molecule's O–H bonds back to the first one's C=O. Two hydrogen bonds close an eight-membered ring: a **cyclic dimer**. The association is stronger and more extensive than in alcohols, and the hydrogen bonds are not broken completely even in the vapour: most carboxylic acids exist as dimers in the vapour phase and in aprotic solvents.

3. A consequence: abnormal molar mass

In benzene, acetic acid is largely dimerised, so a colligative measurement (e.g. freezing-point depression) gives a molar mass of about 120 g/mol, double the true 60 g/mol.

4. Solubility in water

Acids with up to four carbons are miscible with water (they hydrogen-bond with water). Solubility falls as the hydrocarbon part grows; higher acids are practically insoluble, and benzoic acid is nearly insoluble in cold water. Carboxylic acids also dissolve in less polar solvents such as benzene, ether, alcohol and chloroform.

Solved example

Q. Arrange in increasing order of boiling point: propan-1-ol, propanal, ethanoic acid, butane.
A. butane < propanal < propan-1-ol < ethanoic acid (no H-bonding < dipole–dipole < H-bonding < dimeric H-bonding).

Key takeaways

- Two hydrogen bonds join two acid molecules into a cyclic dimer.
- b.p.: acids > alcohols > aldehydes/ketones > alkanes of similar mass.
- Dimers survive in the vapour and in benzene (M measured ≈ double).

- Up to C4 miscible with water; longer chains, less soluble.

Practice questions

1. (MCQ) Which has the highest boiling point? (a) propanal (b) propan-1-ol (c) ethanoic acid (d) butane
2. (MCQ) The number of hydrogen bonds holding an acetic acid dimer together is: (a) 1 (b) 2 (c) 3 (d) 4
3. (MCQ) The molar mass of acetic acid measured in benzene is about: (a) 30 (b) 60 (c) 90 (d) 120
4. (Very short) Up to how many carbons are aliphatic carboxylic acids miscible with water?
5. (Very short) In what form do carboxylic acids exist in the vapour phase?
6. (Short) Why do carboxylic acids boil higher than alcohols of comparable mass?
7. (Short) Why does the solubility of carboxylic acids in water decrease with chain length?
8. (Application) Draw the cyclic dimer of acetic acid and mark the hydrogen bonds.

Answer key

1. (c) ethanoic acid.
2. (b) 2.
3. (d) about 120.
4. Four.
5. Mostly as hydrogen-bonded dimers.
6. Their molecules associate more extensively through hydrogen bonds, forming dimers held by two H-bonds that are not fully broken even in the vapour.
7. The non-polar hydrocarbon part grows, while only the COOH group hydrogen-bonds with water.
8. Two CH_3COOH molecules face each other: O–H···O=C on each side, an eight-membered ring.

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