▶ Video explanation (YouTube Short)

Esterification and Other Reactions of the C–OH Group

In these reactions the –OH of –COOH is replaced: by –OR′ (ester), –Cl (acid chloride), –OCOR (anhydride) or $–NH_2$ (amide) (NCERT 8.9.2). Esters have fruity odours: isoamyl acetate smells of banana, ethyl butanoate of pineapple.

1. Esterification

$RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$ (conc. H_2SO_4 or dry HCl, heat). Example: $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5$ (ethyl acetate) + H_2O. The reaction is reversible: remove water (or ester) as it forms, or use excess alcohol.

2. Mechanism (nucleophilic acyl substitution)

1. H^+ protonates the carbonyl oxygen: $C{=}O^+H$, a more electrophilic carbon.
2. A lone pair of the alcohol's O adds to that carbon; the C=O π pair moves onto the oxygen (tetrahedral intermediate).
3. A proton transfer turns one –OH into $–OH_2^+$, a good leaving group.
4. An –OH lone pair re-forms $C{=}O^+$ as H_2O leaves.
5. Loss of H^+ gives the ester. The oxygen in the water comes from the acid; the alkoxy O comes from the alcohol.

3. Acid chlorides

Reagent	Equation
PCl_5	$RCOOH + PCl_5 \rightarrow RCOCl + POCl_3 + HCl$
PCl_3	$3RCOOH + PCl_3 \rightarrow 3RCOCl + H_3PO_3$
$SOCl_2$ (preferred)	$RCOOH + SOCl_2 \rightarrow RCOCl + SO_2\uparrow + HCl\uparrow$ (both by-products are gases)

4. Anhydrides and amides

$2CH_3COOH \rightarrow (P_2O_5$ or conc. H_2SO_4, heat$) \rightarrow (CH_3CO)_2O + H_2O$. $RCOOH + NH_3 \rightleftharpoons RCOO^-NH_4^+ \rightarrow$ (heat) $\rightarrow RCONH_2 + H_2O$.

Solved example

Q. Why is $SOCl_2$ preferred to PCl_5 for making acid chlorides?
A. Its by-products, SO_2 and HCl, are gases that escape, leaving the acid chloride almost pure.

Key takeaways

- Acid + alcohol ⇌ ester + water (H^+, reversible).
- Mechanism: protonate C=O, alcohol adds, H_2O leaves, $-H^+$.
- $SOCl_2 \rightarrow$ acid chloride; $P_2O_5 \rightarrow$ anhydride; NH_3, heat → amide.

Practice questions

1. (MCQ) $CH_3COOH + C_2H_5OH$ (H^+) gives: (a) ethyl acetate (b) acetaldehyde (c) diethyl ether (d) acetic anhydride
2. (MCQ) The best reagent for RCOOH → RCOCl is: (a) PCl_5 (b) PCl_3 (c) $SOCl_2$ (d) Cl_2
3. (MCQ) In esterification, the oxygen of the water formed comes from: (a) the alcohol (b) the acid (c) H_2SO_4 (d) air
4. (Very short) Name the catalyst usually used for esterification.
5. (Very short) What forms when ammonium acetate is heated?
6. (Short) Why is the carbonyl oxygen protonated first in esterification?
7. (Short) How can the yield of an ester be increased?
8. (Application) Write the steps, with curved arrows, for the acid-catalysed reaction of CH_3COOH with CH_3OH.

Answer key

1. (a) ethyl acetate.
2. (c) $SOCl_2$.
3. (b) the acid.
4. Concentrated H_2SO_4 (or dry HCl).
5. Acetamide, CH_3CONH_2 (+ H_2O).
6. Protonation makes the carbonyl carbon more electrophilic, so the weak nucleophile (the alcohol) can add.
7. Remove water (or the ester) as it forms, or use an excess of alcohol.
8. H^+ on C=O; CH_3OH lone pair to C (C=O π to O); proton shift to make $–OH_2^+$; OH lone pair re-forms C=O as H_2O leaves; $-H^+$: CH_3COOCH_3.

▶ Watch the video explanation