

Carboxylic acids and derivatives (A Level)

A-Level Chemistry 9701 · Topic 33 revision notes

Everything from the 2 lessons of this topic on a few pages: the key idea of each lesson, the diagram to remember, the points to learn and the traps examiners set. Read it, cover it, test yourself.

1. Relative acidity of carboxylic acids

2. Acyl chlorides

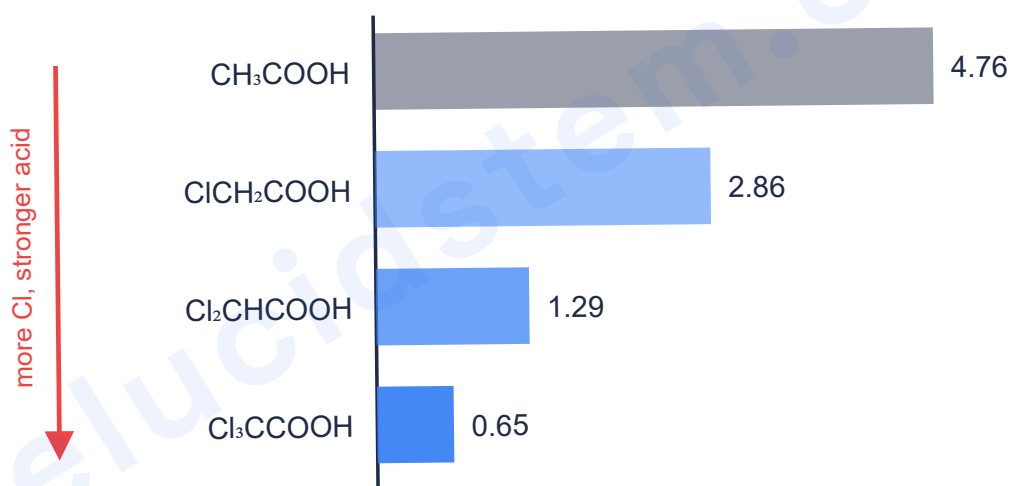
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1 Relative acidity of carboxylic acids

Syllabus 33.1

Carboxylic acids are the strongest of the O-H acids: **carboxylic acid > phenol > water > alcohol**, because the charge of the **carboxylate ion** is shared equally over two O atoms. Anything that stabilises RCOO^- further makes the acid stronger. **Electron-withdrawing** Cl atoms pull electron density away from the COO^- group and spread its charge: the **more Cl atoms**, and the **closer** they are to the COOH group, the stronger the acid (pKa ethanoic 4.76, chloroethanoic 2.86, dichloroethanoic 1.29, trichloroethanoic 0.65). **Electron-donating** alkyl groups destabilise the anion, so ethanoic acid is weaker than methanoic acid. **Methanoic acid**, HCOOH , still has an H on its C=O carbon, so it is oxidised to CO_2 by Tollens', Fehling's and acidified KMnO_4 ; **ethanedioic acid** decolourises warm acidified KMnO_4 , giving CO_2 .

pKa of ethanoic acid and its chloro derivatives (smaller = stronger)



each Cl withdraws electron density and spreads the COO^- charge

Fig. 1: each extra Cl atom lowers the pKa of ethanoic acid

Withdraw electrons, stronger acid.

- ✓ **Order:** $\text{RCOOH} > \text{phenol} > \text{water} > \text{alcohol}$.
- ✓ **More Cl, closer Cl:** lower pK_a , stronger acid.
- ✓ **Alkyl groups:** electron-donating, weaker acid.
- ✓ **Oxidised:** HCOOH (Tollens', Fehling's, KMnO_4) and $\text{H}_2\text{C}_2\text{O}_4$ (warm KMnO_4), both to CO_2 .

Watch out!

Electron-**withdrawing** groups make an acid **stronger**; electron-donating groups make it weaker. The explanation must be about the **stability of the carboxylate anion**, not about the O-H bond alone. More Cl is stronger, and Cl **closer** to the COOH group is stronger. A **smaller** pK_a means a **stronger** acid. Of the simple carboxylic acids, only **methanoic** gives positive Tollens' and Fehling's tests; ethanedioic acid needs **warm** acidified KMnO_4 .

2 Acyl chlorides

Syllabus 33.2

An **acyl chloride**, RCOCl , is made from a carboxylic acid with **PCl_5** (room temperature), **PCl_3 and heat**, or **SOCl_2** . Its carbonyl carbon is bonded to two electronegative atoms, O and Cl, so it is strongly δ^+ and planar, open to attack by nucleophiles. Acyl chlorides react by **nucleophilic addition-elimination**: a lone pair adds to the $\text{C}=\text{O}$ carbon, then the $\text{C}=\text{O}$ reforms and Cl^- leaves with H^+ as **HCl** . With **water** they give the carboxylic acid (vigorous, steamy HCl fumes); with **alcohols and phenols**, esters; with **ammonia and amines**, amides. Ease of hydrolysis: **acyl chloride $\gg$ chloroalkane $>$ chlorobenzene**.

addition-elimination: $\text{CH}_3\text{COCl} + \text{H}_2\text{O}$

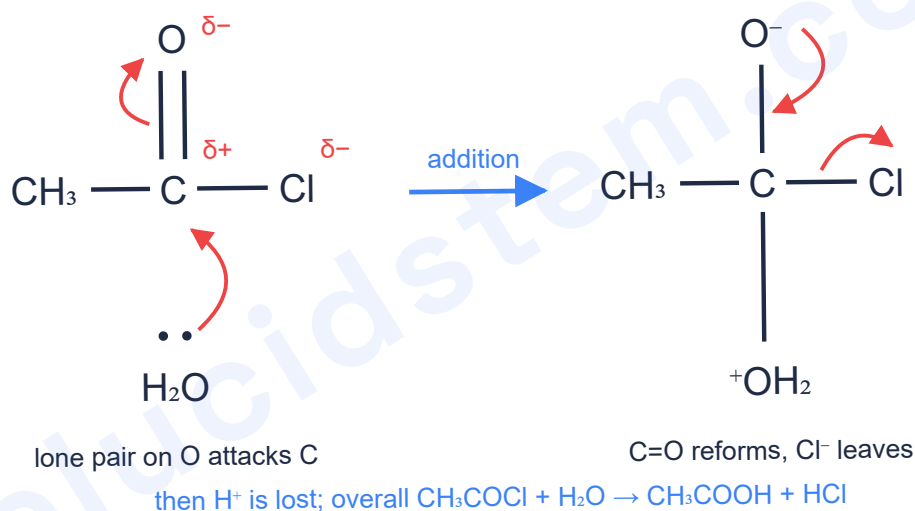


Fig. 1: nucleophilic addition-elimination when water attacks ethanoyl chloride

Very δ^+ carbon, HCl every time.

- ✓ **Make:** $\text{RCOOH} + \text{PCl}_5, \text{PCl}_3$ (heat) or SOCl_2 .
- ✓ **Hydrolysis:** acyl chloride $\gg$ chloroalkane $>$ chlorobenzene.
- ✓ **Products:** water to acid, alcohol or phenol to ester, NH_3 or amine to amide.
- ✓ **Mechanism:** addition (lone pair to C) then elimination (Cl^- leaves).

Watch out!

Show the mechanism in **two steps**: addition (lone pair to C, $\text{C}=\text{O}$ π electrons to O) then elimination ($\text{C}=\text{O}$ reforms, Cl^- leaves). Start every curly arrow from a **lone pair or a bond**, never from an atom or a charge sign. The by-product is always **HCl** (or its ammonium salt), not water. Chlorobenzene is the **hardest** to hydrolyse, not the easiest: its $\text{C}-\text{Cl}$ bond has partial double-bond character.