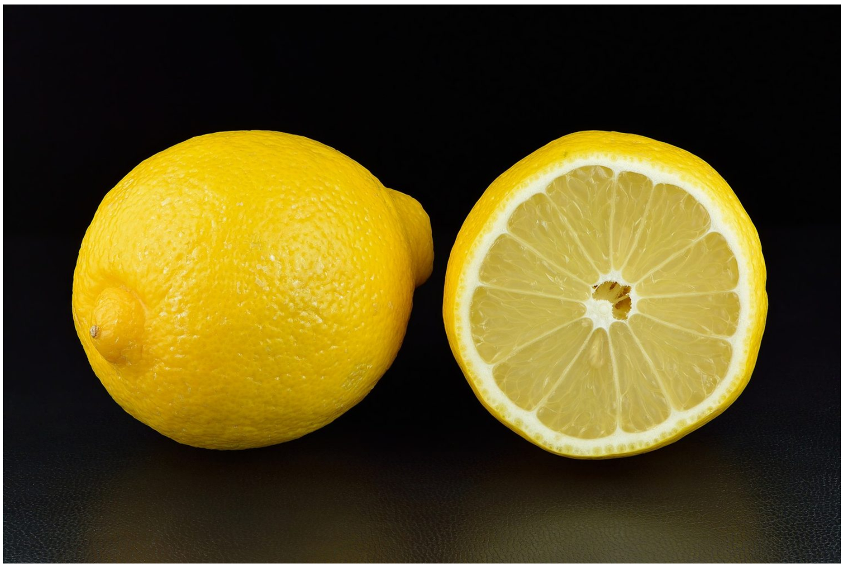
Carboxylic acids and derivatives

A-Level Chemistry

Carboxylic acids



Citrus fruits taste sour because they contain citric acid, a carboxylic acid

Making and reacting

- an **alkylbenzene** 烷基苯 (such as methylbenzene) is oxidised by hot alkaline $KMnO_4$, then dilute acid, to give **benzoic acid** 苯甲酸. The whole side-chain becomes a –COOH group.
- a carboxylic acid reacts with PCl_3 and heat, PCl_5, or $SOCl_2$ to form an **acyl chloride** 酰氯.

Acids that can be oxidised further

Two **carboxylic acids** 羧酸 are special because they can still be oxidised:

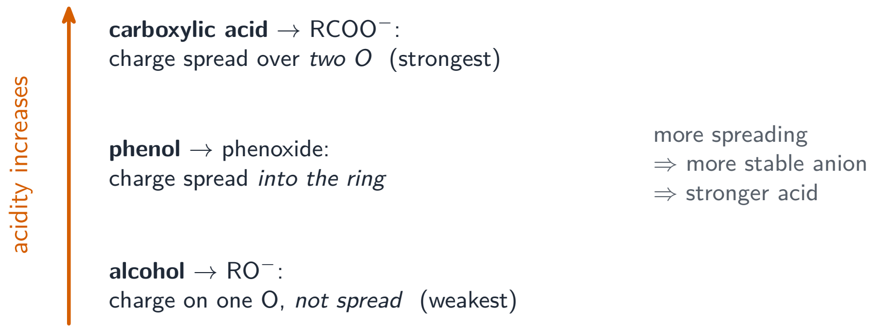
- methanoic acid (HCOOH) is oxidised by Fehling's or Tollens' reagent, or acidified $KMnO_4$ / $K_2Cr_2O_7$, to carbon dioxide and water.
- ethanedioic acid (HOOCCOOH) is oxidised by warm acidified $KMnO_4$ to carbon dioxide.

Relative acidities

The **acidity** 酸性 order is:

$$\text{alcohol} < \text{phenol} < \text{carboxylic acid}$$

A carboxylic acid is the strongest because, when it loses H^+, the negative charge is spread over **two** oxygen atoms, making the ion very stable. In a **phenol** 苯酚 the charge spreads only into the ring, and in an **alcohol** 醇 (giving RO^-) it is not spread at all.



Acidity rises from alcohol to phenol to carboxylic acid: the more the negative charge on the conjugate base is spread out, the more stable the ion and the stronger the acid

Chlorine atoms make a carboxylic acid **more** acidic. Chlorine is **electron-withdrawing** 吸电子: through the **inductive effect** 诱导效应 it pulls electron density away, helping to spread the negative charge and stabilise the ion. So more chlorine atoms (closer to the –COOH) give a stronger acid.

Esters

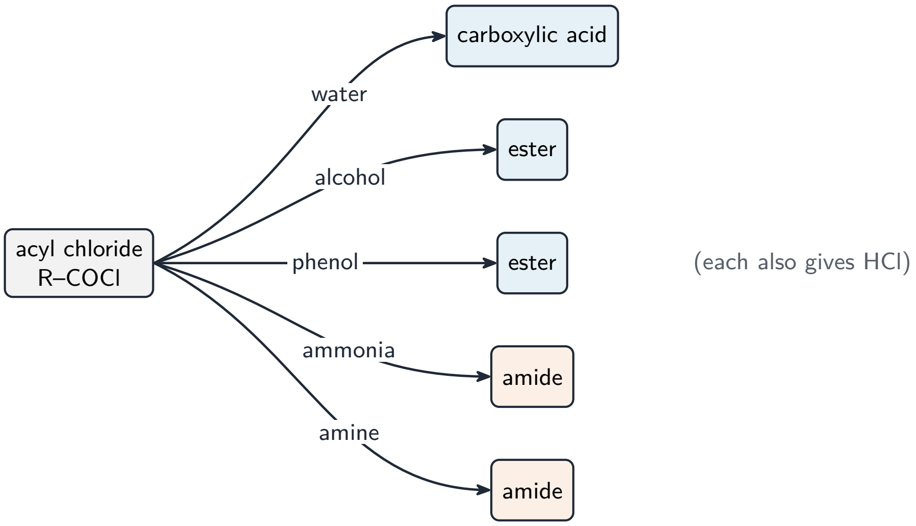
An alcohol (or phenol) reacts with an acyl chloride at room temperature to give an **ester** 酯 and HCl. Examples are ethyl ethanoate (from ethanol) and phenyl benzoate (from phenol).

Aspirin is an ester, made from salicylic acid

Acyl chlorides

Acyl chlorides are made from carboxylic acids (with PCl_3, PCl_5 or $SOCl_2$). They are very reactive. At room temperature they react with:

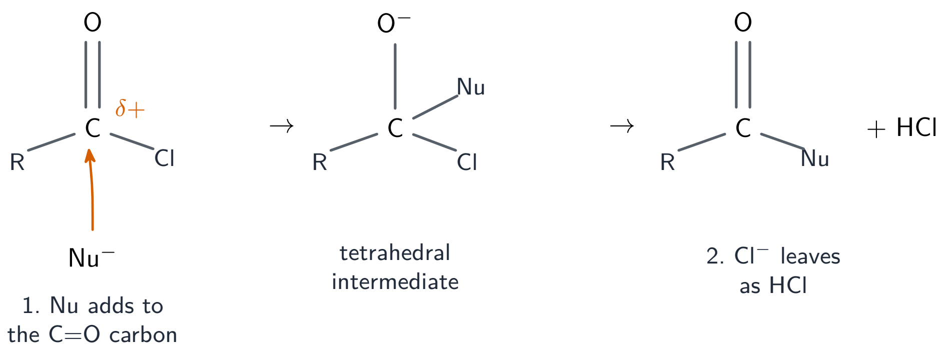
Reactant	Product (plus HCl)
water	the carboxylic acid
an alcohol	an ester
phenol	an ester
ammonia 氨	an **amide** 酰胺
a primary or secondary **amine** 胺	an amide



Acyl chlorides are very reactive: with water, an alcohol, phenol, ammonia or an amine they give the labelled product plus HCl

The addition–elimination mechanism

All these reactions follow an **addition–elimination** 加成消去 mechanism: a nucleophile first **adds** to the slightly positive carbonyl carbon, then HCl is **eliminated**.



Addition–elimination: the nucleophile adds to the δ+ carbonyl carbon, then the C=O reforms and Cl⁻ leaves as HCl

Ease of hydrolysis

Compare how easily three chlorides react with water (**hydrolysis** 水解):

$$\text{acyl chloride} \gg \text{alkyl chloride} \gg \text{aryl chloride}$$

An acyl chloride reacts violently with cold water; an alkyl chloride reacts slowly; an aryl chloride (halogenoarene) does not react, because its C–Cl bond is strengthened by the ring.