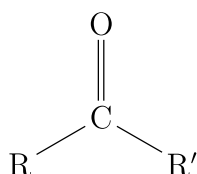


Carbonyls

Definition 0.1 (Carbonyls) — The set of functional groups that contain a C=O bond (a carbon-oxygen double bond).

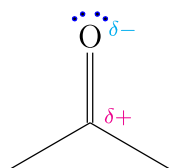
§0.1 Bonding and Structure



Here, the R and R' groups represent other groups which determine what type of carbonyl we are dealing with *e.g.* **ester** or **amide**. The two bonds in the C=O are the σ and the π bond, just like in alkenes.

Because oxygen has 6 electrons around it, there are 4 **non-bonding** electrons, hence there are **two lone pairs** on the oxygen. These make carbonyls good **hydrogen bond acceptors** and so are generally **miscible/soluble** in water.

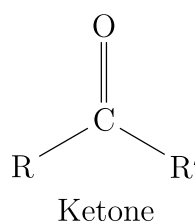
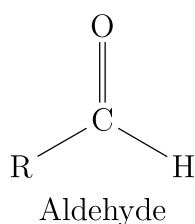
As oxygen is more electronegative than carbon, there is a **dipole** across the bond.



We can identify carbonyls using **infrared** and ^{13}C **NMR** spectra. Most will have the following:

- IR - peak around $1680 - 1830\text{ cm}^{-1}$
- ^{13}C NMR - peak around $160 - 220\text{ ppm}$

§0.2 Aldehydes and Ketones

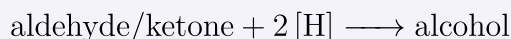


The synthesis of aldehydes and ketones has been previously covered in reactions of alcohols. Aldehydes and ketones can be formed by the **oxidation** of alcohols.

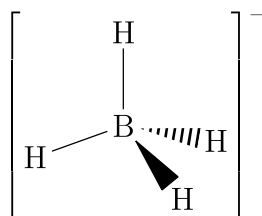
- Aldehydes are produced from the **partial** oxidation of **primary** alcohols.
- Ketones are produced from the complete oxidation of **secondary** alcohols.

The oxidising agent for these oxidations is acidified potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$. In order to tell that the oxidation reaction has occurred, one will observe a colour change from **orange** to **green**.

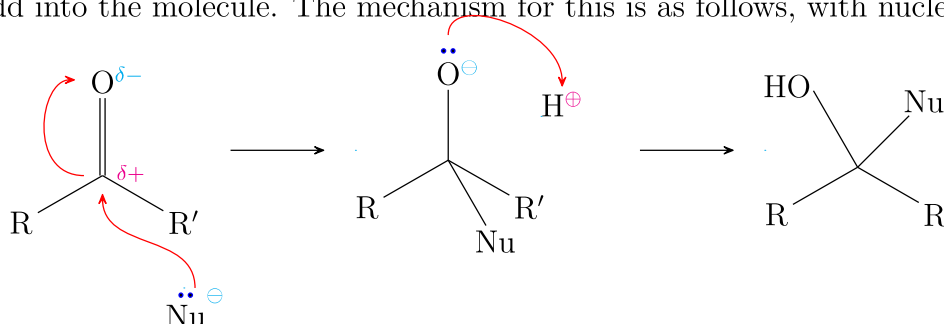
Due to their similar structures, aldehydes and ketones react in similar ways. **Reduction** is the opposite of oxidation, and so can take aldehydes/ketones back to alcohols.

Reaction 0.2 (Reduction of Aldehydes and Ketones)

The most common reducing agent used for this reaction is **sodium tetraborohydride**, NaBH_4 .¹



As the $\text{C}=\text{O}$ bond is **polar**, **nucleophiles** (electron pair donors) can attack the positively charged carbon and add into the molecule. The mechanism for this is as follows, with nucleophile Nu.



Notice how we get an alcohol group present in the organic product after nucleophilic addition of the carbonyl. This is due to the H^+ , which comes about usually because of aqueous conditions - this step is known as **protonation**.

There are two key nucleophiles to be familiar with.

- H^- (hydride ion) - this comes about from the borohydride anion BH_4^-
- CN^- (cyanide ion) - this comes about from potassium cyanide KCN most commonly. N/B: we **do not** use hydrogen cyanide; it is extremely poisonous.

Aldehydes can also undergo further oxidation to carboxylic acids, as we have seen before. There are two main oxidising agents for this:

1. Acidified potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$ with gentle heating.
2. Aqueous mixture of Ag^+ in excess ammonia - Tollen's reagent $\text{Ag}(\text{NH}_3)_2^+$ - with gentle heating (60°C). The oxidation of aldehyde to carboxylic acid simultaneously causes the reduction of Ag^+ to Ag which gives rise to the silver mirror result (see below).

§0.3 Tests for Aldehydes and Ketones

We are concerned with two main reagents: **Tollen's reagent** and **Brady's reagent**. We start with the latter.

Aldehydes and ketones react with **2,4-dinitrophenylhydrazine** (2,4-DNPH), also known as Brady's reagent², to form an **orange precipitate**. No precipitate is formed with other carbonyl compounds such as carboxylic acids or esters.

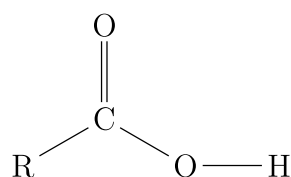
¹Hydrogen gas, H_2 , in the presence of a catalyst can also be used.

²Strictly speaking, Brady's reagent is a solution of 2,4-DNPH in methanol and sulphuric acid.

Functional group	Observation	Result
alcohol	no reaction; stays green	negative
carboxylic acid	no reaction; stays green	negative
ester	no reaction; stays green	negative
aldehyde	orange ppt	positive
ketone	orange ppt	positive

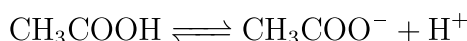
§0.4 Carboxylic Acids

Carboxylic acids have both a carbonyl (C=O) and an O–H bond stemming from the same carbon atom.



Carboxylic acids are both **hydrogen bond acceptors** (lone pairs on both oxygen atoms) and **hydrogen bond donors** (O–H bond), and therefore have higher melting points than aldehydes/ketones.

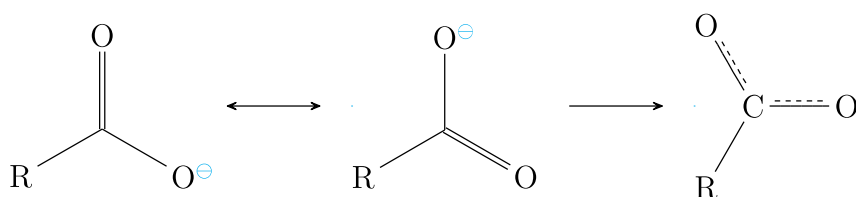
Carboxylic acids are **weak acids** - they do not fully dissociate.



Remark 0.3 It is interesting to note that carboxylic acids are much more acidic than alcohols, even though it is the hydrogen on the O–H that is dissociating. This is because:

1. Negative charges are less stable than neutral atoms.
2. The carbonyl group helps to stabilise the negative charge.
3. The negative charge is ‘shared’ by both oxygen atoms.

The following **resonance structure** shows how it works.

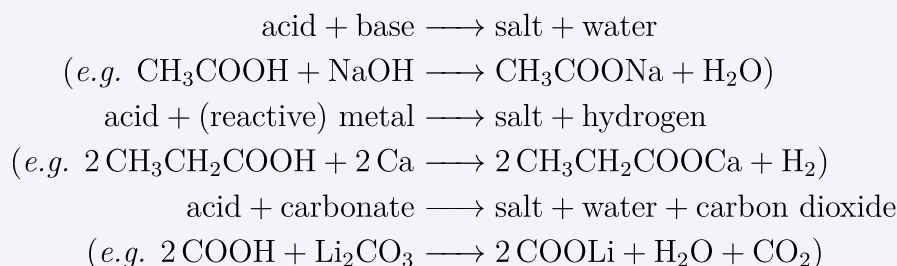


However, we usually draw the negative charge on one oxygen atom for simplicity.

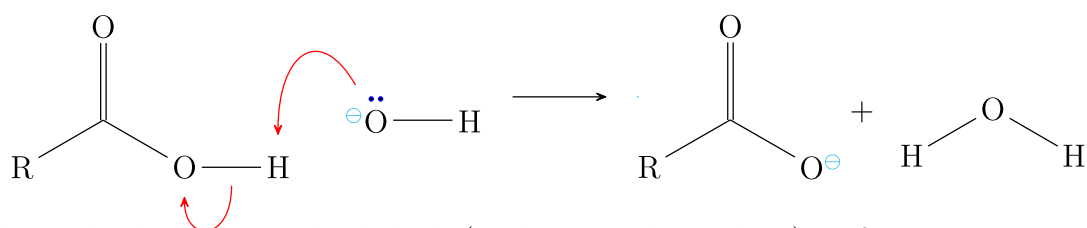
We can identify carboxylic acids using **infrared** with the O–H peak at $3000 - 3300 \text{ cm}^{-1}$ ³, as well as the C=O peak at $1680 - 1830 \text{ cm}^{-1}$.

Carboxylic acids end with the suffix *-anoic acid*, and the **deprotonated** acids (*i.e.* COO^- functional group) end with the suffix *-anoate* - this is the anion part of salts, *e.g.* ‘methanoate’.

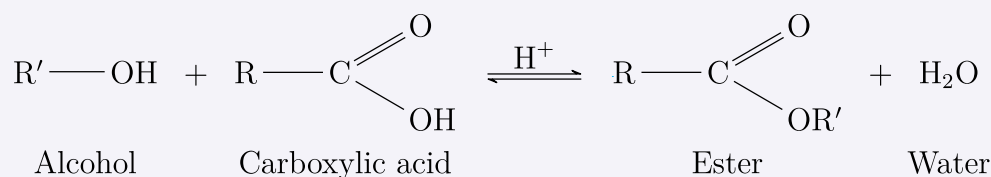
³Note that this is a slightly different value to the peak of the O–H bond in just an alcohol.

Reaction 0.4 (Reactions of carboxylic acids)

We can draw a mechanism for the reaction of a base with a carboxylic acid.



Carboxylic acids also react with alcohols (with an **acid catalyst**) to form esters in a reversible reaction, known as **esterification**.

Reaction 0.5 (Esterification)

From the reactions above, it should be clear that there are many ways to test for carboxylic acids, such as:

- react with carbonate to form CO_2 gas.
- react with an alcohol in acidic conditions, and should produce a fruity smell, due to ester production.⁴

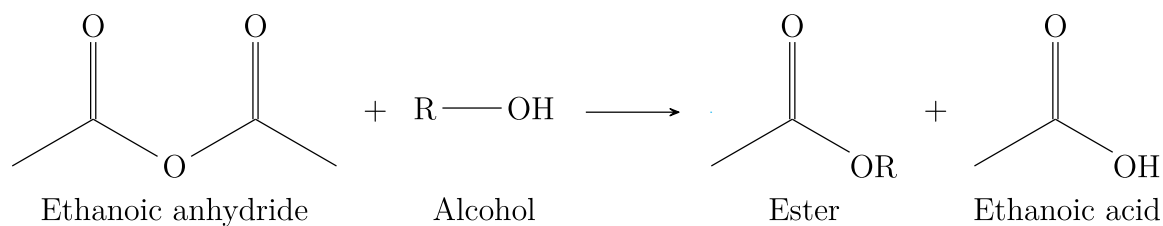
§0.5 Esters

As we have just seen, esters are formed from the reversible reaction 0.5 between carboxylic acids and alcohols.

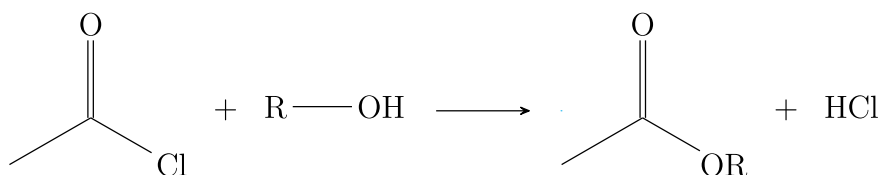
Remark 0.6 It should be made clear that oxygen in the ester (not the one in the double bond) comes from the alcohol, and **not** from the carboxylic acid. In fact, we know this from **isotope labelling** experiments by giving the alcohol ^{18}O and the carboxylic acid ^{16}O , and the ^{18}O atom appears in the final ester.

As water is also produced in the esterification reaction, this reaction is a **condensation** reaction. Esters can also be produced from other carboxylic acid derivatives. For instance, esters can be produced from **acid anhydrides** by reactions with alcohols. The by-product is a carboxylic acid.

⁴Esters have distinctive, sweet smells. This is covered further in the **esters** section.



Esters can also be produced by the reaction of an **acid chloride** with an alcohol. The by-product is HCl.

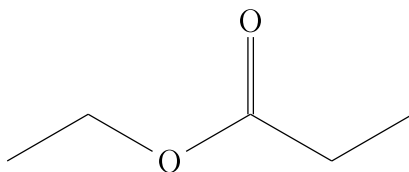


Since the esterification reaction 0.5 is reversible, we can use it to break an ester down into the carboxylic acid and alcohol, by adding an excess of water to shift the equilibrium position to the left side.

Esters are named based on the carboxylic acid part and the alcohol part. The following convention is used:

'alcohol' (+ yl) 'acid' (+ oate)

For example, the following molecule is **ethyl propanoate**.



Simple esters are most commonly used as:

- Fragrances
- Solvents *e.g.* ethyl acetate common in paints and TLC

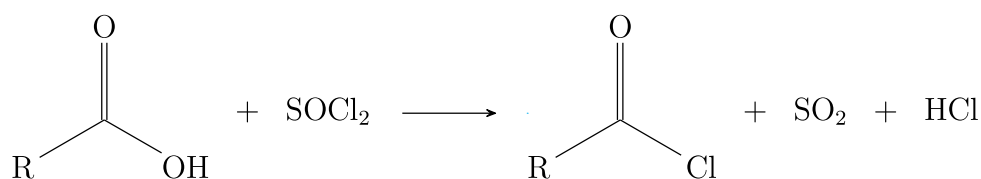
Ester bonds can be found in:

- Synthetic polymers (polyesters)
- Fats (triglycerides)

§0.6 Acid Chlorides

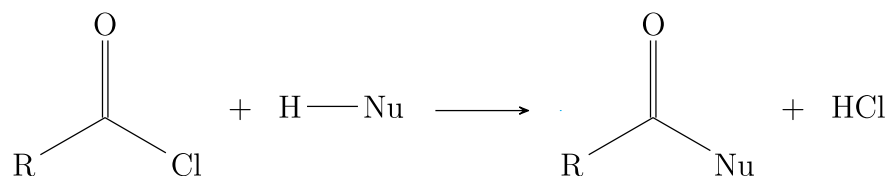
Acid chlorides are the most reactive carboxylic acid **derivative** and can be used to make all other derivatives.

Acid chlorides are produced by the reaction of a carboxylic acid with **thionyl chloride** (SOCl₂) to produce the acid chloride, sulfur dioxide and hydrogen chloride.



Acid chlorides are named in a similar way to carboxylic acids, except the suffix is *-anoyl chloride*, e.g. ethanoyl chloride.

The general reaction of acid chlorides is to substitute the chlorine atoms for other groups.

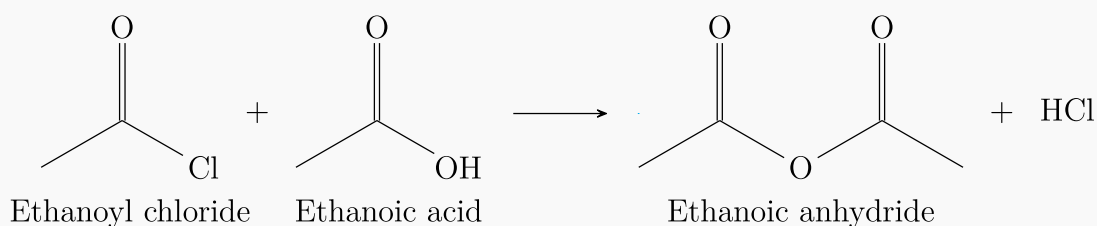


For this reason, acid chlorides are incredibly useful and versatile, if a little hard to control.

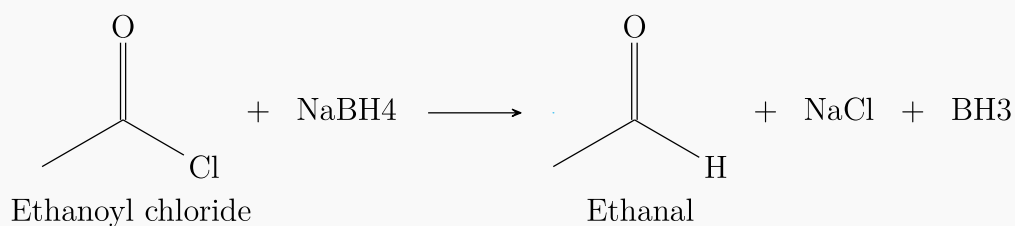
Example 0.7 Write the equation for the reaction between ethanoyl chloride and ethanoic acid, and draw the organic products.

What about ethanoyl chloride and sodium borohydride?

Solution. For ethanoic acid, we have the structure $\text{H}-\text{OOCH}_2\text{CH}_3$, so the nucleophile at play is clearly $^-\text{OOCH}_2\text{CH}_3$. This will replace the Cl atom in the ethanoyl chloride. So we have:



If we instead have NaBH_4 , then we should be familiar that this consists of Na^+ and BH_4^- , which gives rise to the nucleophile H^- . The exception with this however is that we have chloride ions in solution and sodium ions, so these will react, rather than forming HCl. So this gives:



□