# Chapter 15

# Carbonyl chemistry

The carbonyl group crops up a lot in organic chemistry. We are interested in the properties and reactions of the C=O bond. These properties stem from the polarity of the bond; oxygen is more electronegative than carbon, so the electrons in the bond are pulled towards the oxygen leaving it with a $\delta-$ charge. The carbon is left with a $\delta-$ charge, leaving it open to **attack by nucleophiles**[1]. Nucleophiles are things which have a lone pair of electrons (they may be neutral or have a full negative charge, such as $H_2O$ or $Cl^-$ respectively). We can represent the carbonyl group like this: $\underset{\delta+}{\mathrm{C}}\!=\!\underset{\delta-}{\mathrm{O}}$.

## 15.1 Aldehydes and ketones

Aldehydes and ketones both contain a simple C=O moiety. In the case of aldehydes this is terminal (meaning it is at the end of a carbon chain, not that it is fatal), whereas in a ketone it is somewhere in the middle of a chain. They can be represented as RCHO and $R^{'}COR$ respectively. They are nice. You should know how to make them from alcohols from your work in year 12, but that was a long time ago. Aldehydes are the oxidation products of primary alcohols, ketones are the oxidation products of secondary alcohols. This tells you that making an alcohol from a carbonyl compound can be done by reduction. The reducing agent of choice is normally $LiAlH_4$, lithium tetrahydridoaluminate (III).

Aldehydes can be further oxidised to carboxylic acids (RCOOH). Ketones can't. Why?

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[1] The carbon is $\delta+$ meaning that it is a bit positive. In atoms the nuclei are positive. Things that are attracted to positive charge are thus called nucleophiles.

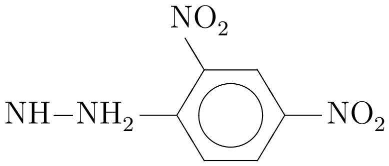
### 15.1.1 Reactions

Aldehydes and ketones with relatively short alkyl chains can dissolve in water. This is because of the formation of hydrogen bonds between the carbonyl oxygen and water molecules. As the hydrocarbon chain gets bigger the solubility of the molecule in water decreases.

Aldehydes react with acidified $\mathrm{Na_2Cr_2O_7}$ solution to produce carboxylic acids. The dichromate is a vivid orange colour at the start of the reaction, but gradually becomes greener as the reaction progresses and the chromium (VI) is oxidised to chromium (III).

When aldehydes are heated with Benedict's solution in alkali we see a red precipitate slowly forming.

We can **test for aldehydes and ketones** by adding Brady's reagent. This contains 2,4-dinitrophenylhydrazine:



One of the lone pairs on the terminal nitrogen of the hydrazine group can act as a nucleophile and attack the carbon of $\underset{\delta+}{\mathrm{C}}{=}\underset{\delta-}{\mathrm{O}}$. This is an addition reaction. Then a water molecule is eliminated from that product forming a vividly-coloured solid.

## 15.2 Carboxylic acids

Why are carboxylic acids acidic? Like all acids an equilibrium is set up between the molecule and the conjugate base / hydrogen ion comination:

$$\mathrm{RCOOH} \rightleftharpoons \mathrm{RCOO^-} + \mathrm{H^+}$$

The $\mathrm{RCOO^-}$ ion is stablised in a similar way to the stabilisation of the phenoxide anion - the negative charge is **delocalised** over the $\mathrm{COO^-}$ part of the molecule. This enables the equilibrium to move to the right (a little bit) and we find that carboxylic acids are generally weak acids.

Like most acids these chemicals can form salts when reacted with a suitable base. This can be seen in the reaction with ammonia which goes like this

$$\mathrm{RCOOH + NH_3 \longrightarrow RCOO^-NH_4^+}$$

and **not like this** (with the ammonia acting as a nucleophile)

$$\mathrm{RCOOH + NH_3 \longrightarrow RCOONH_2 + H_2O}$$

Studies done by electron diffraction have shown that the two bonds in the $\mathrm{RCOO^-}$ ion are the same length. Just like the delocalised ring electrons in benzene these electrons occupy a $\pi$ orbital which is above and below the plane of the COO bit of the molecule.

### 15.2.1 Esters

With non-basic nucleophiles, such as alcohols, carboxylic acids undergo a nucleophilic addition elimination reaction. It is good. Esters smell nice.

$$\mathrm{RCOOH + R'OH \overset{H^+}{\rightleftharpoons} RCOOR' + H_2O}$$

Isotope labelling of the oxygen in the alcohol has shown that the oxygen in the ester product comes from $\mathrm{R^{'}OH}$.

Esters can be turned back into an acid and an alcohol (look at the equilibrium above). Clearly this needs water to make it happen and so it is called **hydrolysis**. This is normally acid or base catalysed (base catalysis produces the salt of the parent acid - try balancing an equation like the lowest one on p 369).

### 15.2.2 Reduction of carboxylic acids

Carboxylic acids can be reduced to the parent alcohol using lithium tetrahydridoaluminate (III) ($\mathrm{LiAlH_4}$). The 'lithal' provides highly nucleophilic hydride ions which attack the $\delta+$ carbon in the $\mathrm{RCOO^-}$ ion. Clearly we can also use $\mathrm{LiAlH_4}$ to reduce aldehydes and ketones to the parent alcohols.

## 15.3 Carboxylic acid derviatives

If we replace the OH in RCOOH with another group we have a carboxylic acid derivative. Hurrah. Putting in an $\mathrm{OR^{'}}$ group gives us an ester; $-Cl$ gives an acyl chloride; $\mathrm{NH_2}$ gives an amide.

### 15.3.1 Acyl chlorides

Acyl chlorides are very reactive. The chlorine atom is strongly electron withdrawing, making the carbon in the carbonyl group particularly attractive to nucleophiles. The chlorine is also a good 'leaving group', meaning that the chloride ions is fairly stable in many solutions.

Acyl chlorides react with water rapidly because the oxygen in water has a lone pair of electrons which can attack the $\delta+$ carbon. The carboxylic acid is generated:

$$\mathrm{RCOCl + H_2O \longrightarrow RCOOH + HCl}$$

Alcohols and amines or ammonia react in exactly analogous ways:

$$\mathrm{RCOCl + R^{'}OH \longrightarrow}$$

$$\mathrm{RCOCl + NH_3 \longrightarrow}$$