5 Functional Group Level _____

A   Introduction

To some students, organic chemistry can seem like a collection of unconnected chemical reactions transforming one functional group to another which just have to be memorised, along with all the conditions and other details.

Of course there are many facets in the interpretation and prediction of organic transformations: we need to consider where the most reactive centres are in a molecule, likely mechanisms and stereochemistry. However, a very useful organising principle when considering reacting carbon atoms in molecules is the one of so-called "functional group level".

The functional group level classifies a single carbon atom in a molecule – typically the one carrying the functional group – depending on the number of bonds it has to an atom or atoms of greater electronegativity than itself. Due to the valency of carbon this number must clearly be an integer in the range 0 to 4. The different levels are named after the simplest possible oxygen-containing functional groups in that level. Some examples are in the table below.

| Name of functional group level	No. bonds to electronegative atoms	Examples
Hydrocarbon	0	Alkanes, alkenes, alkynes, Grignard reagents
Alcohol	1	Alcohols, alkyl halides, amines, thiols, ethers, peroxides
Carbonyl	2	Aldehydes, ketones, imines, acetals, hemiacetals, ketals, hemiketals, hydrates
Carboxylic acid	3	Carboxylic acids, esters, amides, nitriles, acid anhydrides, acid chlorides, ortho esters
Carbon dioxide	4	Carbon dioxide, carbonic acid, urea, carbonate esters, guanidine, carbon disulfide, carbon oxysulfide,

Indeed categorising the carbon atom from any molecule into this scheme is just a trivial case of bond counting. We will see many examples of this in the coming pages.

B   Hydrolysis

One of the most useful features of the functional group level model is the simple rule that hydrolysis of any functional group carbon leads to no change in the functional group level and the transformation of that carbon's functional group to the title functional group of that level.

This is easily visualised by considering the hydrolysis reaction to be exchange for all bonds to more electronegative atoms to be replaced by bonds to −OH. However, when more than one −OH group is bonded to a carbon there is a strong entropic driving force for a molecule of water to be eliminated.

Comparison between the hydrolysis of vic- and gem-dihalides is instructive here. Vic-dihalides have a halogen atom bonded to two adjacent carbon atoms; gem-dihalides have two halogen atoms bonded to the same carbon atoms.
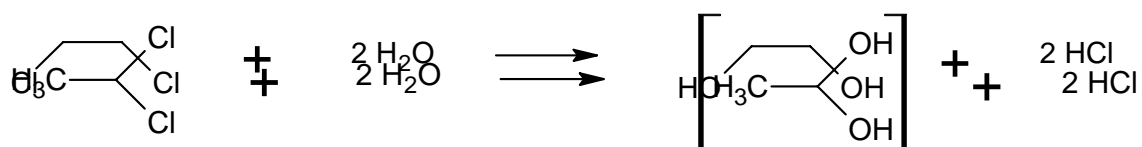

The vic-dihalide gives a diol. Both carbon atoms on the dihalides are in the alcohol functional group as they are both bonded to one electronegative atom, chlorine. Each carbon atoms hydrolyses to give the title functional group of that level, namely the alcohol functional group.
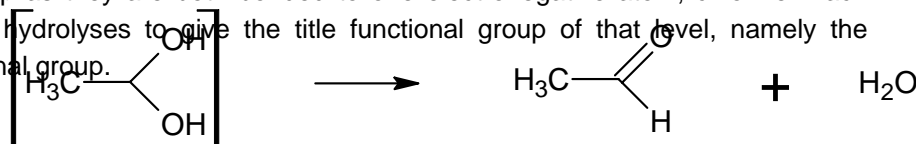
In the case of the gem-dihalide the functional group carbon is in the carbonyl functional group as it has two bonds to electronegative atoms. We imagine these groups to be replaced by −OH groups to give us the compound in brackets. However, this compound is unstable because there is more than one −OH group bonded to a single carbon. This unstable intermediate is shown eliminating a molecule of water in the second step, yielding the final product, ethanal, a carbonyl compound.

C   Classifying functional group interconversions

When a substitution reaction involves the exchange of one electronegative atom bonded to a carbon with another, then there is no change in functional group level. This is usually the case with substitution reactions. A typical example would be the hydrolysis of a halogenoalkane:

$$RCH_2Br + H{-}OH \rightarrow RCH_2OH + HBr$$
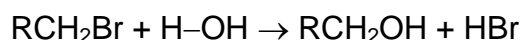
in which the reacting carbon on the bromoalkane remains in the alcohol functional group level during the reaction.

When a reaction causes a carbon to go up in functional group level – in other words when the carbon has more bonds to electronegative atoms in the product molecule than it had in the reactant molecule – then there will have been an oxidation process, and an oxidising agent must have been present. For example, in the chlorination of benzene,
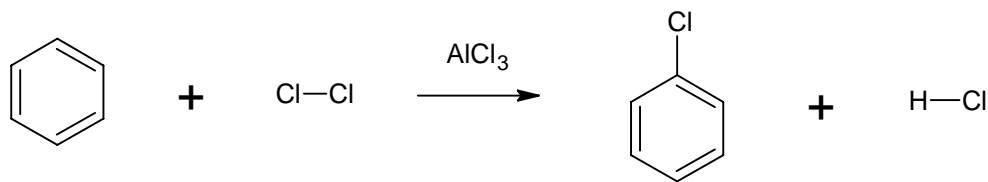
the reacting carbon which forms a bond with a chlorine atom is oxidised up from the hydrocarbon level to the alcohol level.

Similarly when a carbon atom goes down in oxidation level a reduction must have taken place, and a reducing agent must have been present. For example, in the reaction between a nitrile and lithium aluminium hydride, $LiAlH_4$,
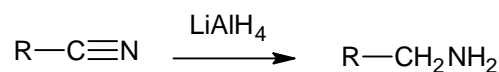

the nitrile carbon is lowered from the carboxylic acid functional group level (three bonds to electronegative nitrogen) to the alcohol level (just one such bond).

There are some functional group interconversions that deserve particular mention to clarify the concept.

1. Reactions involving cyanide ions

Reactions in which an electronegative atom is substituted for a cyanide group, for example:

$$RCH_2Br + NaCN \rightarrow RCH_2CN + NaBr$$
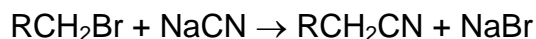
involve a formal lowering of the functional group level of the CH_2 carbon from the alcohol level to the hydrocarbon level. Of course another carbon atom has been introduced into the molecule. This cyanide carbon is in the carboxylic acid functional group level as the carbon has three bonds to a more electronegative atom (nitrogen).

A similar drop in functional group level is observed when hydrogen cyanide undergoes nucleophilic addition to a carbonyl compound,
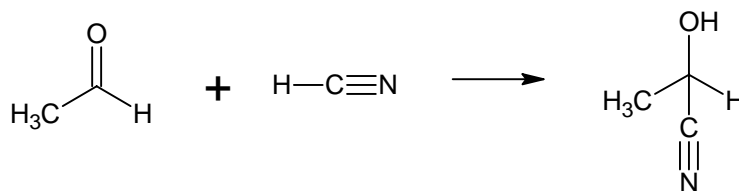

except in this case the functional group level of the reacting carbon in the carbonyl compound goes from the carbonyl level to the alcohol level, as there is now only one bond to an electronegative atom (oxygen) in the product molecule.

2. Addition to alkene addition

Addition reactions are slightly different to the reactions seen so far as two functional group carbons (the carbons of the C=C bond) react at once. There is no rule of thumb: the changes in functional group level of each of the C=C carbons depend what is being added to them. For example, in the hydrogenation reaction

$$H_2C=CH_2 + H–H \rightarrow H_3C–CH_3$$
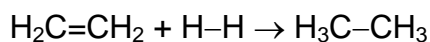
there is no change in any of the carbons' functional group level, since hydrogen is not an electronegative atom. However, in the case of a hydration reaction, such as
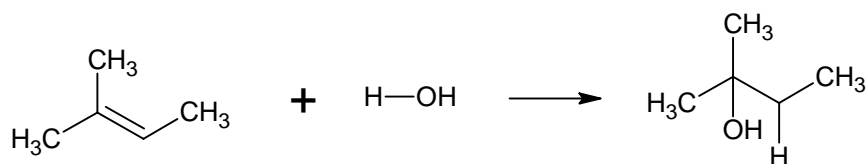
one of the carbon atom's functional group level (the more substituted carbon, which bonds to the oxygen) has increased from the hydrocarbon level to the alcohol level, whereas the other carbon has remained in the hydrocarbon level since it hasn't formed a bond with an electronegative atom (only hydrogen).

In the case of addition of bromine, however, both carbon atoms in the C=C bond go up in oxidation level from the hydrocarbon level to the alcohol level, as they both have a bond to an electronegative atom (bromine) in the product 1,2-dibromoethane.

$$H_2C=CH_2 + Br–Br \rightarrow BrCH_2–CH_2Br$$
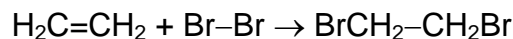
3. Grignard reactions

Grignard reactions lead to carbon-carbon bond formation. The Grignard carbon remains in the same hydrocarbon level as it isn't bonded to any electronegative atoms in either the Grignard reagent or the product of the reaction. The carbon atom that is attacked by the Grignard reagent will go down in functional group level by one level. For example, in the reaction between a Grignard reagent and methanal,

the methanal carbon goes from the carbonyl level to the alcohol level. The Grignard carbon remains in the hydrocarbon level as a methyl group.

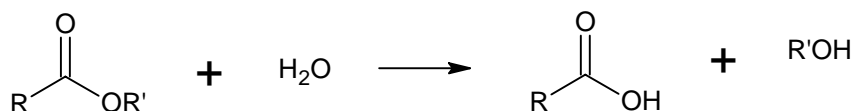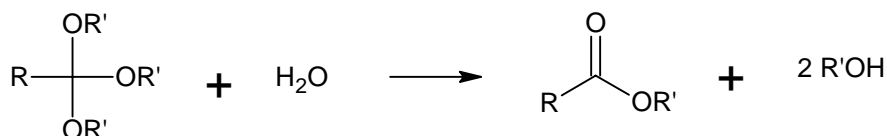## D   Dealing with unfamiliar functional groups

Even with unfamiliar functional groups it is easy work out the functional group level for the functional group carbon atom: just count the number of bonds to a more electronegative element. It is also easy to predict the product of the hydrolysis of that functional group: it's just the title functional group for that particular functional group level.

For example, let us consider ortho ester. The general structure of an ortho ester is shown below.

$$
\begin{array}{c}
\text{OR'} \\
| \\
\text{R}-\!\!\!-\!\!\!-\text{OR'} \\
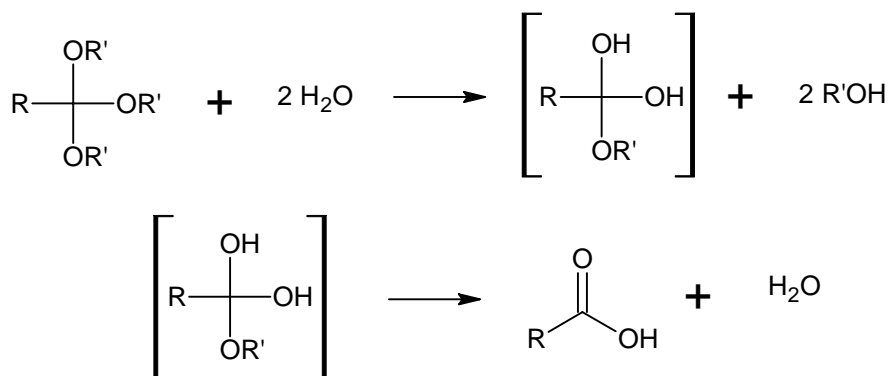| \\
\text{OR'}
\end{array}
$$
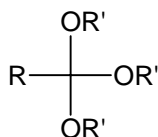
Inspection of the functional group carbon in the above ortho ester reveals that it has three bonds to electronegative oxygen atoms. It is therefore in the carboxylic acid level. Hydrolysis of ortho esters should therefore yield carboxylic acids. This is indeed the case, in a two-step reaction going via an ester:

$$
\begin{array}{c}
\text{OR'} \\
| \\
\text{R}-\!\!\!-\!\!\!-\text{OR'} \\
| \\
\text{OR'}
\end{array}
\; + \; H_2O \; \longrightarrow \;
\underset{R}{\overset{O}{\|}}\!\!-\!\!OR'
\; + \; 2\,R'OH
$$

$$
\underset{R}{\overset{O}{\|}}\!\!-\!\!OR'
\; + \; H_2O \; \longrightarrow \;
\underset{R}{\overset{O}{\|}}\!\!-\!\!OH
\; + \; R'OH
$$

The first of the reactions above is consistent with the ideas discussed in the hydrolysis section. Initially, two of the –OR' groups are replaced by –OH groups, producing the intermediate

$$
\begin{array}{c}
\text{OH} \\
| \\
\text{R}-\!\!\!-\!\!\!-\text{OH} \\
| \\
\text{OR'}
\end{array}
$$
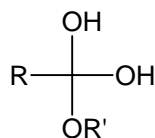
which, having two –OH groups bonded to the same carbon, is unstable and eliminates water to produce the ester. So the first hydrolysis reaction above can itself be considered to proceed in two steps:

$$
\begin{array}{c}
\text{OR'} \\
| \\
\text{R}-\!\!\!-\!\!\!-\text{OR'} \\
| \\
\text{OR'}
\end{array}
\; + \; 2\,H_2O \; \longrightarrow \;
\left[
\begin{array}{c}
\text{OH} \\
| \\
\text{R}-\!\!\!-\!\!\!-\text{OH} \\
| \\
\text{OR'}
\end{array}
\right]
\; + \; 2\,R'OH
$$

$$
\left[
\begin{array}{c}
\text{OH} \\
| \\
\text{R}-\!\!\!-\!\!\!-\text{OH} \\
| \\
\text{OR'}
\end{array}
\right]
\; \longrightarrow \;
\underset{R}{\overset{O}{\|}}\!\!-\!\!OH
\; + \; H_2O
$$

The two steps above sum to give the equation for the first hydrolysis reaction.

E   Teaching strategies

Some teachers may wish students to be presented with functional group interconversions in the traditional fashion, and only to consider the functional group level approach later on as a means of unifying the organic chemistry covered.

At the beginning of a Pre-U course, students will be aware of some functional group interconversions from their previous chemistry course, and so should in fact be ready to meet the functional group level concept level early on – after all, it is a very simple construct. In fact, students' pre-existing organic chemical knowledge could be neatly revised while framing it in the functional group level approach. This could be a useful way to begin a Pre-U course at the start of the sixth form.

F   Sample exercises

1   Ethanamide is a simple example of an amide.

(a)   Draw the structure of ethanamide showing the geometry of the molecule.

[2]

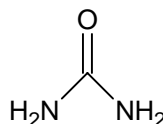(b)   What is the functional group level of the amide group?

…………………………………………………………………………………………….[1]

Amides may be hydrolysed by reaction with dilute acid to give a carboxylic acid.

(c)   Write an equation for the hydrolysis of ethanamide.

……………………………………………………………………………………… [2]

Urea, shown below, might be thought of as a diamide, though in fact its chemistry is quite distinctive.

(d)   What is the functional group level of the carbon atom in urea?

……………………………………………………………………………………… [1]

(e)   Write an equation for the hydrolysis of urea.

……………………………………………………………………………………… [2]

The structure of guanidine is shown below.
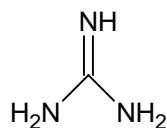
(f)   What is the functional group level of the carbon atom in guanidine?

        ……………………………………………………………………………… [1]

(g)   What are the products of hydrolysis of guanidine?

        ……………………………………………………………………………… [2]

2   The structures below may look unfamiliar. Use your knowledge of functional
        group levels to work out the following for each.

(a)   the functional group level of the carbon atom indicated by the arrow

(b)   the product of hydrolysis of the species

(c)   the chemical equation for the hydrolysis