Chem Factsheet

www.curriculum-press.co.uk Number 176

Functional Group Levels

Organic chemistry can sometimes seem like a long list of chemical reactions transforming one functional group to another, which just have to be memorised, along with all the reagents and conditions necessary to bring about the changes.

One approach that can help to make sense of this potentially confusing 'jumble' is that of 'Functional Group Level' (FGL). The FGL classifies a single carbon atom in a molecule – usually the one carrying the functional group – depending on the number of bonds it has to atoms of greater electronegativity than itself.

Due to the ability of carbon to form four covalent bonds with neighbouring atoms this must be 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	Number of bonds to electronegative atoms	Examples
Hydrocarbon	0	Alkanes, alkenes, alkynes
Alcohol	1	Alcohols, halogenoalkanes, amines, thiols, ethers, peroxides
Carbonyl	2	Aldehydes, ketones
Carboxylic acid	3	Carboxylic acids, esters, amides, nitriles, acid anhydrides, acid chlorides
Carbon dioxide	4	Carbon dioxide, carbonic acid, urea, carbon disulfide

Hydrolysis Reactions:

One of the most useful features of the FGL model are the simple rules that:

1. hydrolysis (splitting by reaction with water) of any functional group carbon leads to no change in the FGL.
2. hydrolysis changes a carbon atom's functional group to the **title functional group** of that level. For example, hydrolysis of a halogenoalkane forms an alcohol.

This is easily visualised by considering the hydrolysis reaction to be the exchange of all bonds to more electronegative atoms for bonds to –OH.

However, when more than one –OH group is bonded to a carbon there is a strong tendency for a molecule of water to be eliminated.

Comparison between the hydrolysis of vic (1,2-) and gem (1,1-) dihalides is instructive here. Vic-dihalides have halogen atoms bonded to two **adjacent** carbon atoms; gem-dihalides have two halogen atoms bonded to the **same** carbon atom.

e.g. $ClCH_2CH_2Cl + 2H_2O \rightarrow HOCH_2CH_2OH + 2HCl$

The vic-dihalide ($ClCH_2CH_2Cl$) gives a diol. Both carbon atoms on the dihalides are in the alcohol functional group level as they are each bonded to one electronegative atom, chlorine. Each carbon atom hydrolyses to give the title functional group of that level, namely the alcohol functional group.

In the case of the gem-dihalide (CH_3CHCl_2) the functional group carbon is in the carbonyl FGL 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.

$$CH_3CHCl_2 + 2H_2O \rightarrow [CH_3CH(OH)_2] + 2HCl$$

However, this compound is unstable because there is more than one –OH group bonded to a single carbon. This unstable intermediate eliminates a molecule of water in the second step, yielding the final product, ethanal, a carbonyl compound.

$$[CH_3CH(OH)_2] \rightarrow CH_3CHO + H_2O$$

Substitution Reactions

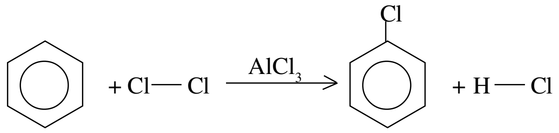
When a substitution reaction involves the exchange of one electronegative atom bonded to a carbon with another, then there is no change in FGL. This is usually the case with substitution reactions. A typical example would be the hydrolysis of a halogenoalkane.

$$RCH_2Br + H{-}OH \rightarrow RCH_2OH + HBr$$

In this case the reacting carbon in the bromoalkane remains in the alcohol FGL.

Oxidation Reactions

When a reaction causes a carbon to go up in FGL – in other words when the carbon in the product has more bonds to electronegative atoms 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, as it has gone from zero bonds to more electronegative atoms to one bond to a more electronegative atom.

Reduction Reactions

Similarly when a carbon atom goes down in FGL 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, $LiAlH_4$,

$$R—C \equiv N \xrightarrow{LiAlH_4} R—CH_2NH_2$$

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

There are some functional group inter-conversions that deserve particular mention to clarify the concept.

Reactions involving Cyanide Ions

Reactions in which an electronegative atom is substituted by a cyanide group such as:

$$RCH_2Br + NaCN \rightarrow RCH_2CN + NaBr$$

involve a lowering of the FGL of the CH_2 carbon from the alcohol level (one bond to electronegative bromine) to the hydrocarbon level (now bonded to another carbon). 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 FGL is observed when hydrogen cyanide undergoes nucleophilic addition to a carbonyl compound,

$$CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$$

except in this case the functional group level of the reacting carbon in the carbonyl compound goes from the carbonyl level (2 bonds to the electronegative oxygen) to the alcohol level (only one bond to electronegative oxygen) in the product molecule.

Alkene Addition Reactions

These addition reactions are slightly different to the reactions seen so far as two 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 on what is being added to them. For example, in the hydrogenation reaction

$$H_2C{=}CH_2 + H\text{-}H \rightarrow H_3C\text{-}CH_3$$

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

$$CH_2{=}CHCH_3 + H_2O \rightarrow CH_3CH(OH)CH_3,$$

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 has only formed a bond with another 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.

$$H_2C{=}CH_2 + Br–Br \rightarrow BrCH_2–CH_2Br$$

Even with unfamiliar functional groups it is easy work out the FGL 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.

Oxidation States

Since functional group atoms are usually more electronegative than carbon there are some parallels between functional group level and oxidation state and also some important differences.

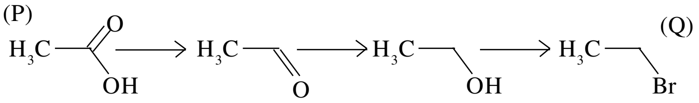
When dealing with the oxidation state of an element in a compound where a molecule of the compound contains more than one atom of that element, the oxidation state is the average of the oxidation states of the element in the separate atoms. In the case of carbon compounds, the important carbon atom is the one bonded to the functional group of interest, and so the FGL approach just concentrates on this important atom. For example, using oxidation states, carbon has a different oxidation state in methane (-4), ethane (-3) and propane (-8/3) (which is one reason why we tend to think of organic redox reactions in terms of loss or gain of oxygen or hydrogen rather than in terms of loss or gain of electrons). It is more meaningful, chemically, to classify these hydrocarbons in the same level, as we do in the functional group level approach.

In the FGL approach the only bonds that are considered are the bonds to atoms from other elements present in the functional group. This is because these are the atoms that determine the chemical properties of the molecule. Hydrogen bonded to carbon is much less important in the chemistry of organic molecules, which is why it is neglected in the FGL approach. The oxidation state approach explicitly considers these hydrogen atoms, which complicates the chemical picture unnecessarily.

Practice Questions

Some examples of Pre-U type questions are given below to allow you to practise applying the concept of FGL.

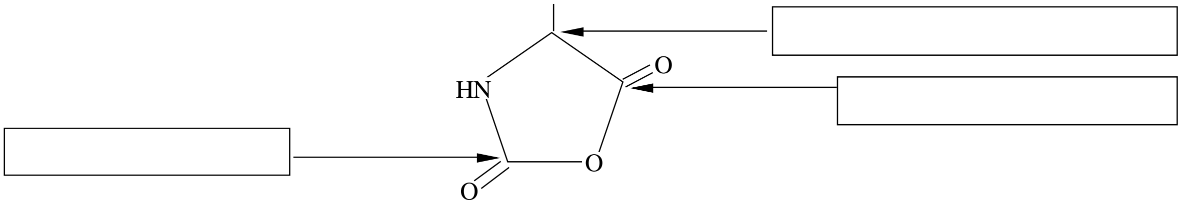
1. Compound P is converted to compound Q in three steps.



What is the overall change in functional group level of the carbon atom of the COOH group of P in this reaction scheme?
A no change B 1 level C 2 levels D 3 levels E 4 levels

2. Carbon oxysulfide, COS, has been detected in emissions from volcanoes. It has recently been suggested that it played an important role in the formation of the first peptides from prebiotic amino acids. The structure of COS is shown: S=C=O

(a) State the functional group level of the carbon in COS. [1 mark]
(b) COS helps the formation of the peptide linkages through the initial formation of a cyclic compound X, shown below. COS and the amino acid react in a 1:1 ratio.On the structure of X below, identify the functional group level of each of the carbons indicated by an arrow. Assume R is an alkyl group [3marks]



(c) Suggest an equation for the reaction of COS with water [1mark]

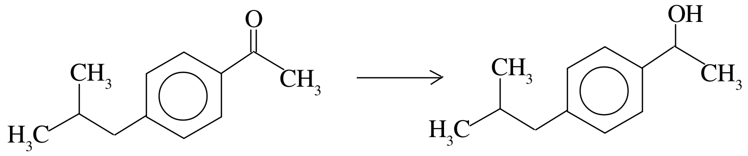
3. In the laboratory, lactic acid can be synthesised from ethanal in two steps.

Step 1: $CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$
ethanal 2-hydroxypropanenitrile

Step 2: $CH_3CH(OH)CN + 2H_2O + H^+ \rightarrow CH_3CH(OH)COOH + NH_4^+$
lactic acid

(a) Describe the changes in functional group level in steps 1 and 2. [2 marks]
(b) What type of reaction is step 2? [1 mark]

4. One of the stages in the Hoechst process for the manufacture of Ibuprofen is shown



With reference to the concept of functional group level explain what type of reaction is taking place in this conversion [3 marks]

Answers

1. Option C is correct as, at the start, the arrowed carbon is in the carboxylic FGL with 3 bonds to electronegative atoms, while, at the end of the sequence, it is in the alcohol FGL with only one bond to an electronegative atom.
2. (a) Carbon dioxide level/ level 4 as there are four bonds to electronegative atoms
(b)
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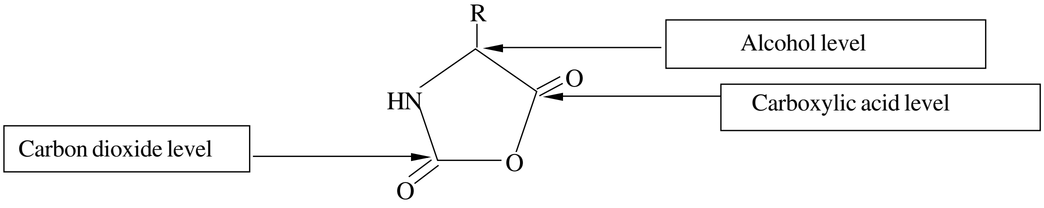

(c) Reaction with water is hydrolysis so the product will be the 'title' compound of the FGL, i.e. CO_2
$COS + H_2O \rightarrow CO_2 + H_2S$

3. (a) In step one the reacting carbon changes from the carbonyl level (with two bonds to electronegative oxygen) to the alcohol level (with one bond to electronegative oxygen).
In step two the reacting (nitrile) carbon stays at the carboxylic acid level with the 'change' being from three bonds to nitrogen to three bonds to oxygen atoms.
(b) No change in FGL means that this change is not a redox reaction and must therefore be hydrolysis.
4. The carbonyl FGL carbon in the reactant changes DOWN to the alcohol FGL so this must be a reduction reaction.

Acknowledgements: *This Factsheet was researched and written by Tony Tooth.* ***Curriculum Press, Bank House, 105 King Street, Wellington, Shropshire***