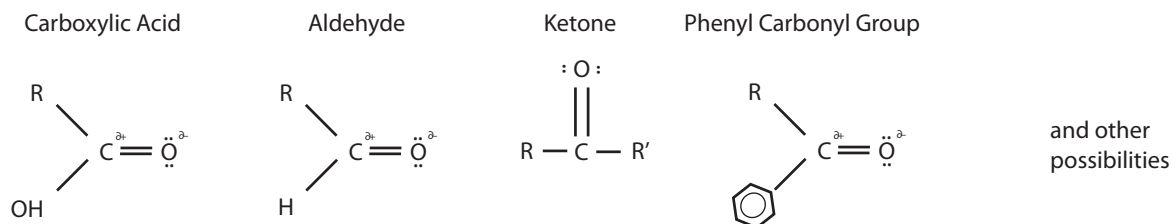


A Second Year blog on Carbonyl Compounds: Part 1 on Acids, 12th Jan 2019

(There is a considerable amount of **revision** in this blog. The material is in the Second Year Organic Book.)

Next to Benzene, Carbonyl compounds are probably the second most examined topic in 'A' Level Organic Chemistry. Carbonyl compounds have the form " $RR'>C=O$ " (where "R" and "R'" are any legitimate species, and the ">C=" conveys a C atom with 4 bonds, with one of them being a double bond), and Carbonyl compounds typically include Carboxylic Acids/ Aldehydes/ Ketones/ Esters/ Amides/ Acyl Chlorides/ Acid Anhydrides/ and Phenyl Carbonyl compounds (second from right below)/etc. NB Anything that has the form " $RR'>C=O$ " will have the " $C^{\delta+}=O^{\delta-}$ " configuration in it.



This is how Chemistry LibreTexts shows some of the Carbonyl compounds. (An "Enone" is an Alkene conjugated to a Ketone. It does **not** form any part of the UK 'A' Level syllabus.) The symbol "X" is very often used to represent a Halogen species.

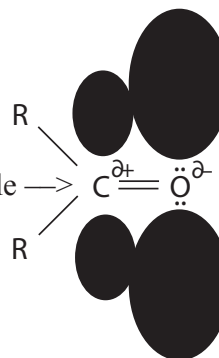
Compound	Aldehyde	Ketone	Formaldehyde	Carboxylic Acid	Ester	Amide	Enone	Acyl Halide	Acid Anhydride
Structure									
General Formula	RCHO	RCOR'	CH ₂ O	RCOOH	RCOOR'	RCONR'R''	RC(O)C(R')CR''R'''	RCOX	(RCO) ₂ O

Please remember that you cannot write Aldehydes as ending in "-OH" because that would convey the impression that they were alcohols. **Aldehydes (RCHO) have to be written as ending in "-HO"**.

Ignoring the extra stability possessed by Benzene, there is very little chance of a *nucleophile* reacting with Benzene because Benzene is physically surrounded (both above and below) by a large delocalised π ring. With an Alkene there is a bit more opportunity for nucleophilic attack because the protection is not quite so encompassing; but with both Benzene and an Alkene there is no question – **reactions that occur do so mainly as electrophilic reactions**. However, when it comes to Carbonyl compounds the situation is the *opposite*. **In general, carbonyl compounds are subject to NUCLEOPHILIC attack/reactions.**

Carbonyl Compounds

This δ^+ flank is left exposed to an attack by a nucleophile \rightarrow



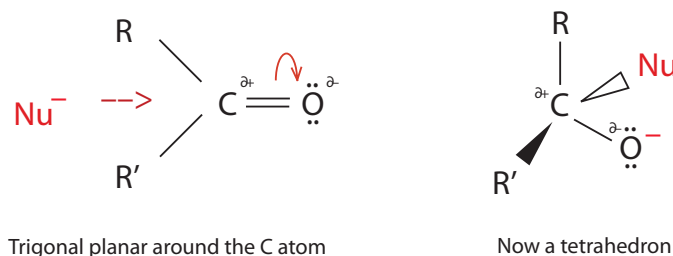
← The black bit is meant to represent electron density.

It does not matter what form the nucleophile takes. It is a **nucleophile** if it is

- an electron rich species (that has a full “-” charge, or else a partial “ δ^- ” separation of charge)
- that reacts with a species that contains an electron deficient area (a “+” / a “ δ^+ ” area / an empty orbital)
- by **donating** a pair of electrons to that species, and
- forming a (dative) covalent bond with that species.

In essence, a nucleophile is a donor of a pair of electrons (and indeed a nucleophile is often termed a Lewis base).

Technically, the movement of electrons should be shown by curly arrows, but I have drawn it here with a straight arrow. You can thus see that the Nu^- is attacking the $\text{C}^{\delta+}$ atom, and a **nucleophilic addition reaction** is about to take place in which the double bond will break heterolytically (and the C atom will then be attached to four species instead of to three species).



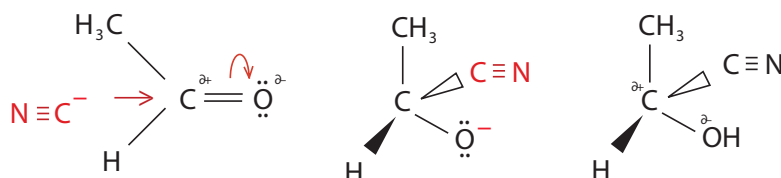
Please note that (even though I have not shown all the steps in the mechanism) that

- i) the negative charge has moved from the nucleophile to the O atom, and
- ii) that if the nucleophile had “n” C atoms in it, then the species on the right would now have “n” more C atoms in it than it previously had. (**“n” C atoms will have been added to the molecule.**)

For example, if the nucleophile were a “ CN^- ” species from HCN where

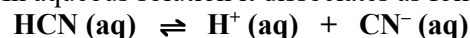


then this is what would happen (*with the “ H^+ ” from the HCN joining on in the last step*).

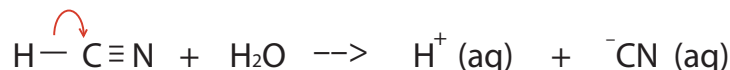


The substance above has changed from an **Aldehyde** (Ethanal) to a **Nitrile** (2-hydroxy propanonitrile), and from a two-Carbon chain (**ethanal**) to a three-Carbon chain (an hydroxy**propanonitrile**).

HCN goes under the guise of different names viz. Hydrogen Cyanide/Hydrocyanic Acid/and Prussic Acid, and it is a very weak acid. In aqueous solution it dissociates as follows



but the negative charge is actually on the C atom and not on the N atom¹. You can see this if you draw HCN in its aqueous form.



¹ I did warn you that we chemists are not as robust scientists as Mathematicians and Physicists are. You could **not** get away with this sort of sloppiness in Maths. If you were to put your negative signs in the wrong place in Maths all your answers would be wrong – *and yet we do it all the time in Chemistry*. It makes me quite ashamed to be a chemist.

Let me start by reminding you about **Carboxylic Acids** (and most Carboxylic acids are *weak* acids).

- According to **Arrhenius'** definition, an Acid is a substance that in aqueous solution neutralises an alkali to produce water.



- However, some Acid-Base² reactions do not produce any water, therefore the definition had to be broadened to take this into account, and accordingly the **Brønsted–Lowry** definition of an Acid became

An Acid is a proton donor / A base is a proton acceptor

- and the great Gilbert **Lewis** then broadened the definition still further and said
An Acid is a substance that accepts a pair of electrons / A base is an electron pair donor

The change in definition did not change any of the reactions themselves. It just meant that a larger 'set' of reactions came under the definition each time that the definition was altered.

Generally speaking, an acid

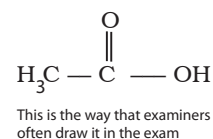
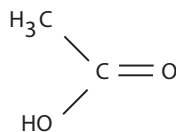
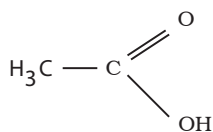
- dissociates protons (H^+)
- often reacts with a base to form WATER and ionic salts ($\text{H}^+ + \text{OH}^- \longrightarrow \text{H}_2\text{O}$), but
- any proton donor is an acid and any proton acceptor is a base (some acid/base reactions do not form water therefore *the formation of water is not an essential component of an acid-base reaction*)
- a compound/a substance that is an acid (and the generic form of an acid is written as "HA") will have a cationic species that consists of a dissociable H^+ , and also an anionic species (A^-) that can accept a proton
- a *dilute* acid is one that has been diluted with water and this should not be confused with
- a **weak acid** which when it dissociates its protons reaches a position of dynamic equilibrium when only a relatively small proportion of its protons have been dissociated, whereas
- a **strong acid** is one which when it dissociates its protons reaches a position of dynamic equilibrium when a large proportion of its protons have been dissociated – and a *very strong* acid is one where the dissociation goes to completion and there are no or virtually no non-dissociated protons left and where the reaction cannot be reversed (because the ions are fully separated/surrounded by water molecules)
- a strong acid will be associated with a weak conjugate base and a weak acid will be associated with a strong conjugate base, and
- it does not matter whether an acid is strong or weak, so long as there is something that is absorbing/ reacting with the protons that are being dissociated, then the acidic substance will keep on dissociating its protons **until there are no more protons left to dissociate**, and finally
- in its most general sense, a base can be considered to be a lone pair donor (this being the contribution of the great Gilbert Lewis), and thus **in Organic Chemistry a nucleophile is a Lewis acid**.

In short, when a Carboxylic Acid is dissolved in Water it will dissociate a proton onto a water molecule to form $\text{H}_3\text{O}^+(\text{aq}) / \text{H}^+(\text{aq})$ (just as an Inorganic acid does), and this will react

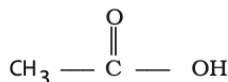
- with some metals to produce $\text{H}_2(\text{g})$
- with $\text{CaCO}_3(\text{s})$ to produce $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$
- with an Hydroxide to produce Water plus a salt, etc.

A Carboxylic Acid fits neatly with all these descriptions, where the "Carboxylic" bit means that the acids are Carbon based species. There are many ways to draw a Carboxylic Acid, and on the next page I have shown three ways for drawing Ethanoic Acid.

² An "alkali" is a soluble "base".



Technically speaking, in bond line diagrams, the methyl/ethyl/propyl/etc species should be *drawn* with the **Carbon atom next to the bond line** – but many scientists do not do so, and they (legitimately) draw the bond line diagram as follows. (The “–COOH” bit is the characteristic of a Carboxylic Acid.)



or this could be written as “R–COOH”.

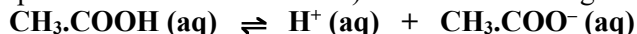
Functionally a Carboxylic Acid is the same as a non-Carboxylic Acid. The main difference between a non-Carboxylic Acid and a Carboxylic Acid is that **most** Carboxylic Acids are weak acids. Let us therefore look at this aspect of Carboxylic Acids.

The strength of an Acid

In Brønsted–Lowry terms an acid is a species that dissociates protons, and a strong acid is one that dissociates all or virtually all of its protons (viz. Hydrochloric Acid, Nitric Acid, Sulfuric Acid, Hydrobromic Acid, Hydroiodic Acid, Perchloric Acid, and Chloric Acid) so much so that the reaction with water can be written as a **reaction to completion** e.g.



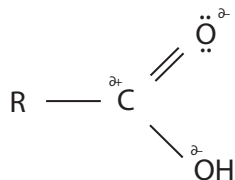
whereas a weak acid is one that is formed as a result of a reversible reaction where the position of dynamic equilibrium lies very far to the left (viz. dynamic equilibrium is reached when only a very small proportion of the available protons has been dissociated) and it is written e.g.



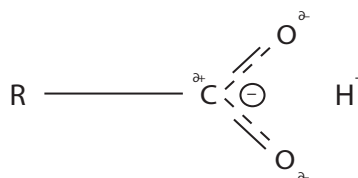
The way that your understanding of this will be tested in the exams is to ask you about relative strengths of acids.

- You could be given the pKa value of different acids, and then asked why they have pKa values of that *relative* magnitude, or
- you could be asked to list some acids that you have been given in the order of the strength of the acids and the answer that the examiners are looking for is almost always in terms of the **increase** in electron density or the **reduction** in electron density that is created in the “–CO^{δ-}O^{δ-}” bit of the acids involved (the area enclosed by the dashed lines in the right hand diagram below).

Two of the Resonance forms of a Carboxylic Acid



The dashed line indicates the delocalisation of the electron in the acid.



The greater the electron density that there is in the “–CO^{δ-}O^{δ-}” area, then the more tightly will the H⁺ be held, **and the harder will it then be for the H⁺ proton to be dissociated**. I will come back to this in a few moments' time.

The most common species that **PUSHES** electron density onto another species is the **Alkyl Group** (i.e. $-C_nH_{2n+1}$), whereas there are many species that ‘suck’ electron density off other species – and this is nearly always determined by a differential in electronegativity. **A more electronegative species will always PULL electron density off a less electronegative species** (that being the definition of electronegativity).

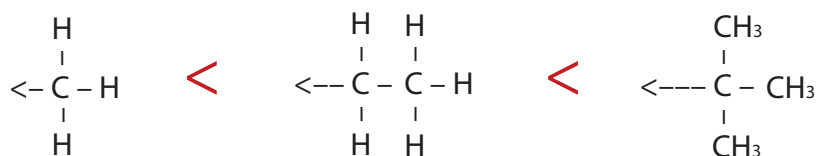
Species that PUSH electron density onto another species

If an Alkyl Group pushes electron density, then it must follow that two Alkyl Groups will push more electron density, and three Alkyl Groups will push even more electron density and four will push yet more and so on. This feature is commonly expressed as



where “ \leftarrow ” stands for “is pushing electron density”, and
“ $<$ ” stands for the normal usage of “less than”
and “ $-C_4H_9$ ” therefore pushes more electron density than “ $-C_3H_7$ ”.

I drew those species in a straight line, but I could have drawn it differently viz.



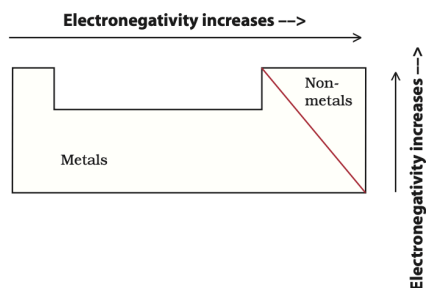
OK, the larger the number of alkyl groups the greater will be the amount of electron density that is being pushed, and the more electron density that there is at the end of the line, the smaller will the ability of the H^+ proton to be dissociated (**and the weaker will the acid thus be**). **The WEAKER that an acid is, the SMALLER the proportion of its protons that it will dissociate.**

Numerically, the smaller the pKa value of an acid, the smaller will its pH value be (and the STRONGER will it be as an acid): the smaller the pKa / the smaller the pH the STRONGER the acid.

Species that suck electron density off other species

There is literally a huge number of species that suck electron density off other species, and it is entirely to do with the difference in electronegativity. In a Periodic Table, electronegativity increases

- across each Period, and
- up each Group.



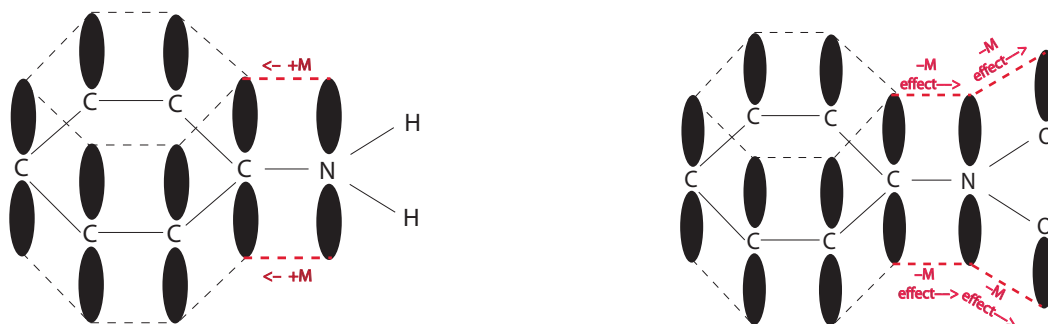
If you keep the rules at the bottom of page 5 in mind, then it does not take much to work out which species will pull more electron density and which will pull less – and please remember that **the more electron density that is withdrawn, the less tightly will the H⁺ proton be held and the stronger will the acid become.**

For example, “—>CH₂Cl” will withdraw less electron density than will “—>CHCl₂”, and in turn it will pull/withdraw less electron density than “—>CCl₃”. Using the symbols that we used earlier,

“—>CH₂Cl” < “—>CHCl₂” < “—>CCl₃” and

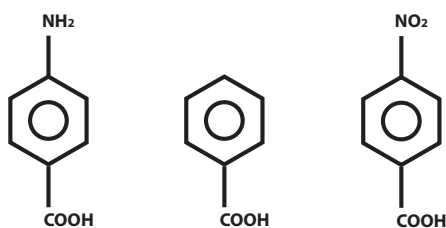
“—>CH₂Cl” < “—>CH₂N” < “—>CH₂O” < “—>CH₂F” etc.

What I have described is pretty straightforward. It is only when you introduce phenyl species that it begins to become slightly more complicated – but all you have to do is to remember the +M and the –M effect that we talked about in the third blog on Benzene (29th December 2018) and it will become very clear. The comparison between C₆H₅.NH₂ (Phenylamine/Aniline/) and C₆H₅.NO₂ (Nitrobenzene) makes it clear.



How will the strength of these three acids therefore compare?

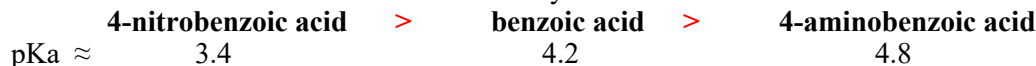
4-aminobenzoic acid benzoic acid 4-nitrobenzoic acid



Ask yourself

- which acid has had more electron density pulled off the “—CO^{δ-}O^{δ-}” bit of it, and therefore
- which acid is holding on less tightly to its H⁺ proton, and
- which acid will dissociate more of its protons, and thus
- which is the stronger acid?

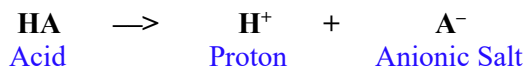
This used to be called a “no-brainer” because you did not have to have a brain to work out that



where “>” means “is a stronger acid than”.

(NB The smaller the pKa, the **stronger** the acid and the smaller the pH, the **stronger** the acid.)

The generic form of an acid is



and the Hydrogen atom *in an acid* is acting like a metal³. It is not possible to compare exactly like for like, but here are some rules that will help you to decide which acid is stronger than another acid, HA₁ or HA₂, where A₁ and A₂ can be either single atoms (such as HCl) or a species (such as H₂SO₄, or C₆H₅COOH). Please remember that if a species holds on to its proton more tightly then it will be a **weaker** acid, and if it holds on less tightly it will dissociate the proton more easily and be a **stronger** acid.

HA₁ is a stronger acid than HA₂ if

1. **HA₁ and HA₂ are roughly the same size, and if A₁ is more electronegative than A₂.**

I have shown below the bonding pair of electrons as a surrogate for the electron cloud. Because A₁ is more electronegative than A₂, A₁ has drawn the electron cloud much closer to itself, and this allows H⁺ to be dissociated more easily from HA₁ than is the case with HA₂, and this makes HA₁ the **stronger** acid.



2. **A₁ is physically larger than A₂.** Remember the 1/(distance)² effect, and here d₁ > d₂ therefore A₁'s hold on its proton is much *less* than A₂'s hold on its proton (because the greater distance diminishes the “hold”) and **strengthens/increases** the acidity.

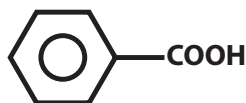


The **closer** that H is to its anion, the **weaker** will the acid will be.

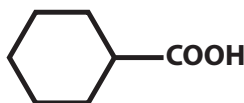
H is closer to A₂ therefore it is held more tightly by A₂ than by A₁. HA₂ is thus the **weaker** Acid.

3. **A₁ has resonance stability but A₂ does not.** C₆H₅.COOH has a pKa of 4.2 while C₆H₁₁.COOH has a pKa of 4.8.

A₁ is a stronger acid than A₂ because it has a delocalised structure and it is therefore **more stable** than A₂.



Benzoic Acid, C₆H₅COOH

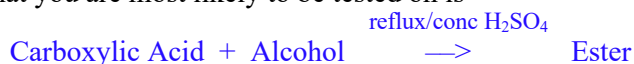


Cyclohexane-carboxylic Acid, C₆H₁₁.COOH

and there are other rules, but I do not want to make the thing too complicated.

³ Even though it is **not** a metal, sometimes Hydrogen does act like a metal (metals like to give up their electrons to non-metal elements e.g. NaCl → Na⁺ + Cl⁻).

This Blog has been a Revision blog on Carboxylic Acids. To get more information on Carboxylic Acids, please read Chapter 21 and 21A of the Second Year book on Organic Chemistry. The reaction involving a Carboxylic Acid that you are most likely to be tested on is



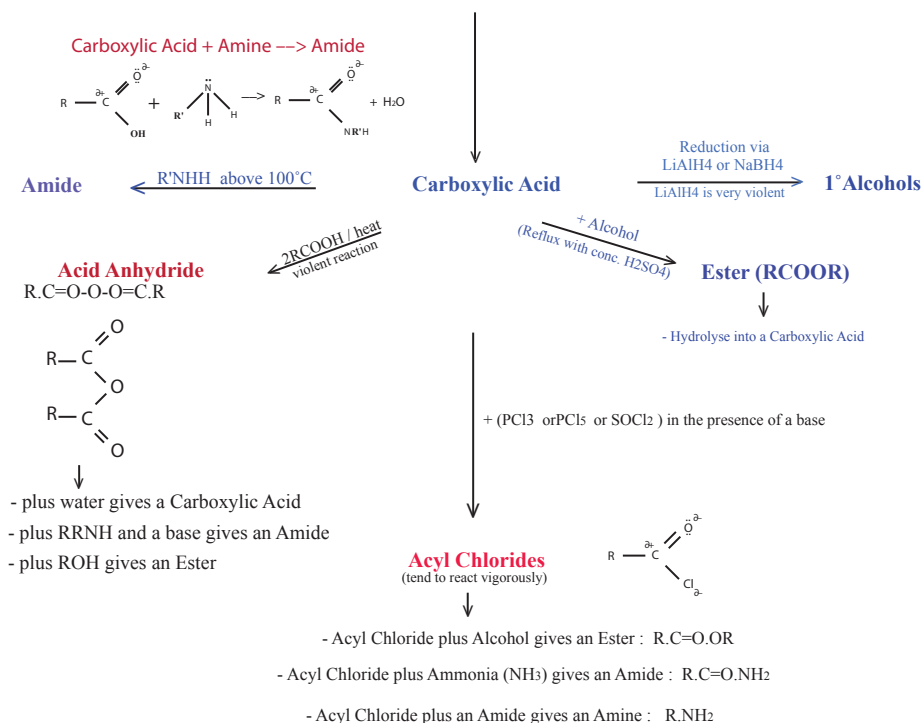
Below is an info tree on Carboxylic Acids. The reactions in blue are the ones that you are most likely to get in the UK 'A' Level exams. You never know what they are going to give you in the exams these days, so I have given you more than you (theoretically) need. Please remember that since Mr Gove's (post-2015) changes, you can be given an extremely complicated species that is not in the Syllabus, and whilst you are not expected to know anything about the species itself, you **are** expected to recognise the underlying functional groups within the species, and then be able to apply your knowledge of those functional groups to analyse the likely reactions of the complicated species.

Routes into a Carboxylic Acid

THE MAIN ROUTES 1° Alcohol plus Potassium Dichromate and conc. Sulphuric Acid (Heat)

Nitrile plus HCl plus water
 Reflux an **Amide** with H^+ and Water
 Acyl Chloride plus Water
 Acid Anhydride plus Water

THE MINOR ROUTES Tollen's/Fehling's/Benedict's also oxidise Aldehydes into Carboxylic Acids The Triodomethane reaction with a methyl Carbonyl compound will produce a Carboxylic Acid and CH_3



Please remember that whilst a Carboxylic Acid will react with an Alcohol in the presence of a strong acid to form an Ester and Water, so also an Ester can be hydrolysed back into a Carboxylic Acid and an Alcohol in the presence of a strong acid. The reaction is thus a reversible one. The conversion to an Ester is thus better performed in the presence of a strong base (rather than a strong acid), and then HCl added to create the Carboxylic Acid. The base reaction is not a reversible one.

NB The reactions of a Carboxylic acid as just an ordinary acid, albeit a weak one, have been ignored.