

Year 2, Organic Chemistry, Chapter 21A:

Determination of the Strengths of Carboxylic Acids

NB There are many factors that affect the ease of dissociation of a proton from a substance, but for 'A' Level, the only factors that I shall consider here are electronegativity and charge density.

$$K_c = \frac{\text{The product of the concentrations of the Products to their stoichiometric ratios}}{\text{The product of the concentrations of the Reactants to their stoichiometric ratios}}$$

- Please remember that the molecules of a **strong** acid will dissociate all (or nearly all) of their protons and that therefore
 - a strong acid will have a LARGE K_a (where $K_a = K_c \cdot [H_2O] = K_c \times 55.5$) because, by definition, a strong acid dissociates a large proportion of its constituent protons, therefore $[H^+]$ and [its constituent base] will be large – thus giving a large K_c and a large K_a .

and, $pK_a = -\log_{10}(K_a)$ therefore

- a large K_a will give a **small** pK_a .¹
- Let me start with some Maths.
- The general equation for an acid dissolved in Water² is
$$HA + \text{Water} \rightleftharpoons H^+(aq) + A^-(aq)$$

Therefore the

$$K_c = \frac{[H^+].[A^-]}{[HA].[H_2O]}$$

but $[H_2O] = 55.5$ (55.5 recurring as I have shown on e.g. page 5 of Year 2/Chapter 1/Inorganic)

$$\text{and } K_c.[H_2O] = K_c \times 55.5 = K_a$$

therefore

$$K_a = \frac{[H^+].[A^-]}{[HA]}$$

and

$$pK_a = -\log_{10}(K_a)$$

- The pK of Water is better known as $pK_w = 14$ at $25^\circ C / 298K$.³
- *All of the above is just revision from Year 2, Inorganic Chemistry, but let me remind you of how you derive K_w .*

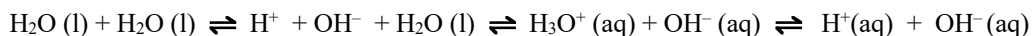
¹ cf. Chapters 3/4/5/6 of Year 2, Inorganic Chemistry, Equilibrium Constants.

² Please remember that you can get an acid dissolved in many different things.

³ The Dissociation Constant of Water, $K_w = [H^+].[OH^-] = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ at 298K.

The Equilibrium Ionic Product of the Water Constant, K_w

- The reaction equation for the dissociation of pure water is



therefore the K_c for pure Water at a given temperature is

$$K_c = \frac{[\text{H}^+(\text{aq})] [\text{OH}^- (\text{aq})]}{[\text{H}_2\text{O (l)}]}$$

and just as with K_a , since $[\text{H}_2\text{O (l)}]$ is just a number (which at 298K is “55.5”), the Equilibrium Ionic Product of the Water Constant, K_w , at equilibrium at a given temperature can be and is defined as

$$K_c \cdot [\text{H}_2\text{O (l)}] = K_w = [\text{H}^+(\text{aq})] \cdot [\text{OH}^- (\text{aq})]$$

- The K_c for pure water at 298K is almost exactly 1.8×10^{-16} therefore (ignoring the units)

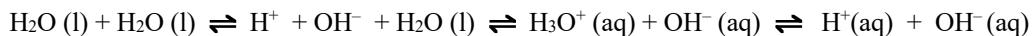
$$K_w = K_c \cdot 55.5 \approx 1.8 \times 10^{-16} \times 55.5 \approx 1 \times 10^{-14} \quad \text{at 298K}$$

and, since the stoichiometric ratio of $\text{H}_2\text{O (l)} \rightleftharpoons \text{H}^+ (\text{aq}) + \text{OH}^- (\text{aq})$ is 1 : 1 : 1, $[\text{H}^+] = [\text{OH}^-]$
 $\therefore [\text{H}^+(\text{aq})] = 1 \times 10^{-7} \text{ mol dm}^{-3}$, and $[\text{OH}^- (\text{aq})] = 1 \times 10^{-7} \text{ mol dm}^{-3}$, therefore

$$K_w = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} = [\text{H}^+(\text{aq})] \cdot [\text{OH}^- (\text{aq})] \approx (1 \times 10^{-7} \text{ mol dm}^{-3}) \cdot (1 \times 10^{-7} \text{ mol dm}^{-3})$$

$$\text{or } [\text{H}^+]^2 = [\text{OH}^-]^2 = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}, \quad \text{and} \quad [\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ mol dm}^{-3}$$

- These are all very important relationships so please take the time to make sure that you can reconstruct them for yourself from first principles. Start with



and then work out every single line in the logic on this page until you get to

$$[\text{H}^+]^2 = [\text{OH}^-]^2 = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}, \quad \text{and} \quad [\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ mol dm}^{-3}$$

$$\text{p}K_w = -\log_{10}(1 \times 10^{-14}) = 14$$

- From the above, it is also true that if $K_w = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} = [\text{H}^+(\text{aq})] \cdot [\text{OH}^- (\text{aq})]$

$$\begin{aligned} \text{then } -\log_{10}(K_w) &= -\{ \log_{10}[\text{H}^+] + \log_{10}[\text{OH}^-] \} \\ &= -\log_{10}[\text{H}^+] + (-\log_{10}[\text{OH}^-]) \end{aligned}$$

$$\text{therefore } \text{p}K_w = \text{pH} + \text{pOH} = 14.$$

- OK, now let us get back to the determination of the strengths of Carboxylic Acids. **What is it that makes a Carboxylic Acid weak or strong?**

NB Last year I told you that all Carboxylic Acids are weak. That is not true. It was a First Year oversimplification, as we shall see.

- Methane with four “C–H” bonds is not acidic, but Methanol with three “C–H” bonds and one “C–OH” bond is *mildly acidic*, and the same is true no matter how many Carbon atoms there are in the molecule. *Why is this so?*
- The difference in negativity between a Carbon atom and a Hydrogen atom is $(2.5 - 2.1 =) 0.4$, whereas the difference in electronegativity between an Oxygen atom and a Hydrogen atom is much larger at $(3.5 - 2.1 =) 1.4$. Oxygen is the second most electronegative element in the Periodic Table and its atoms pull electron density off Hydrogen atoms onto themselves and there is then a considerable separation of charge in the “ $O^{\delta-} - H^{\delta+}$ ” bond. The H atom, denuded of its electron density, is thus not quite “free” to wander off, but it is certainly a tiny bit inclined to wander off if it spots a ‘base’ which has a lone pair of electrons attached to it. (Please remember that a “base” is a **proton acceptor** or a **lone pair donor**.)
- Phenol, $C_6H_5.OH$, is an Alcohol (it is the simplest of all the Alcohols of Benzene), but it is more acidic than the Alkyl Alcohols (i.e. substances with the form $C_nH_{2n+1}.OH$), and Carboxylic Acids are even more acidic than Phenol, and Halogenation makes all of these species more acidic still. *So what is going on?*
- The figures below are the **pKa** values at 298K and NOT the **pH** Values. Please therefore do not think to yourself “Ah yes. pH of 1 therefore a strong acid.” They are not pH values. They are not Ka values. They are **pKa** values (and the smaller the pKa value, the stronger the Acid).



<u>Substance</u>	<u>Acidity</u>	<u>pKa value</u>
Di-chloroethanoic Acid	Strong acid	1.29
Sulphuric Acid	Strong acid	1.92
Chloroethanoic Acid	Weakish acid	2.86
<i>(this used to be called chloroacetic acid)</i>		
Methanoic Acid	Weak acid	3.75
<i>(this used to be called formic acid)</i>		
Benzoic Acid	Weak acid	4.20
Ethanoic Acid	Very weak acid	4.76
<i>(this used to be called acetic acid)</i>		
Butanoic Acid	Very weakly acid	4.82
2-methylpropanoic Acid	Very weakly acid	4.85
Propanoic Acid	Very weakly acid	4.87
<i>(this used to be called proprionic acid)</i>		
tri-methyl ethanoic Acid	Very weakly acid	5.05
Phenol	Not very acidic	10.00
Water	Neutral	14.00
Methanol	Hardly acidic at all	15.50

and if you look at the table on page 4 (it comes from University of California, Santa Barbara), then you will see how these values fit in with those on this page.

- The dissociation of protons from an acid can be measured in aqueous solution (i.e. when the acid is dissolved in water) or quite often it is measured in DMSO (DiMethylSulphoxide) because DMSO dissolves both polar and nonpolar substances (whereas Water dissolves polarised substances but finds it difficult to dissolve non-polar substances).

Table of Acids with Ka and pKa Values*

CLAS

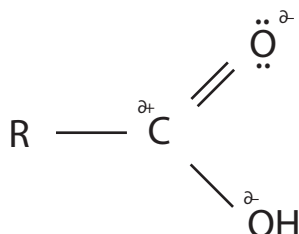
Acid	HA	A ⁻	Ka	pKa	Acid Strength	Conjugate Base Strength		
Hydroiodic	HI	I ⁻	Strong acids completely dissociate in aq solution (Ka > 1, pKa < 1). Conjugate bases of strong acids are ineffective bases.					
Hydrobromic	HBr	Br ⁻						
Perchloric	HClO ₄	ClO ₄ ⁻						
Hydrochloric	HCl	Cl ⁻						
Chloric	HClO ₃	ClO ₃ ⁻						
Sulfuric (1)	H ₂ SO ₄	HSO ₄ ⁻						
Nitric	HNO ₃	NO ₃ ⁻						
Hydronium ion	H ₃ O ⁺	H ₂ O	1	0.0				
Iodic	HIO ₃	IO ₃ ⁻	1.6 x 10 ⁻¹	0.80				
Oxalic (1)	H ₂ C ₂ O ₄	HC ₂ O ₄ ⁻	5.9 x 10 ⁻²	1.23				
Sulfurous (1)	H ₂ SO ₃	HSO ₃ ⁻	1.54 x 10 ⁻²	1.81				
Sulfuric (2)	HSO ₄ ⁻	SO ₄ ²⁻	1.2 x 10 ⁻²	1.92				
Chlorous	HClO ₂	ClO ₂ ⁻	1.1 x 10 ⁻²	1.96				
Phosphoric (1)	H ₃ PO ₄	H ₂ PO ₄ ⁻	7.52 x 10 ⁻³	2.12				
Arsenic (1)	H ₃ AsO ₄	H ₂ AsO ₄ ⁻	5.0 x 10 ⁻³	2.30				
Chloroacetic	CH ₂ ClCOOH	CH ₂ ClCOO ⁻	1.4 x 10 ⁻³	2.85				
Citric (1)	H ₃ C ₆ H ₅ O ₇	H ₂ C ₆ H ₅ O ₇ ⁻	8.4 x 10 ⁻⁴	3.08				
Hydrofluoric	HF	F ⁻	7.2 x 10 ⁻⁴	3.14				
Nitrous	HNO ₂	NO ₂ ⁻	4.0 x 10 ⁻⁴	3.39				
Formic	HCOOH	HCOO ⁻	1.77 x 10 ⁻⁴	3.75				
Lactic	HCH ₃ H ₅ O ₃	CH ₃ H ₅ O ₃ ⁻	1.38 x 10 ⁻⁴	3.86				
Ascorbic (1)	H ₂ C ₆ H ₆ O ₆	HC ₆ H ₆ O ₆ ⁻	7.9 x 10 ⁻⁵	4.10				
Benzoic	C ₆ H ₅ COOH	C ₆ H ₅ COO ⁻	6.46 x 10 ⁻⁵	4.19				
Oxalic (2)	HC ₂ O ₄ ⁻	C ₂ O ₄ ²⁻	6.4 x 10 ⁻⁵	4.19				
Hydrazoic	HN ₃	N ₃ ⁻	1.9 x 10 ⁻⁵	4.72				
Citric (2)	H ₂ C ₆ H ₅ O ₇ ⁻	HC ₆ H ₅ O ₇ ²⁻	1.8 x 10 ⁻⁵	4.74				
Acetic	CH ₃ COOH	CH ₃ COO ⁻	1.76 x 10 ⁻⁵	4.75				
Propionic	CH ₃ CH ₂ COOH	CH ₃ CH ₂ COO ⁻	1.34 x 10 ⁻⁵	4.87				
Pyridinium ion	C ₅ H ₄ NH ⁺	C ₅ H ₄ N	5.6 x 10 ⁻⁶	5.25				
Citric (3)	HC ₆ H ₅ O ₇ ²⁻	C ₆ H ₅ O ₇ ³⁻	4.0 x 10 ⁻⁶	5.40				
Carbonic (1)	H ₂ CO ₃	HCO ₃ ⁻	4.3 x 10 ⁻⁷	6.37				
Sulfurous (2)	HSO ₄ ⁻	SO ₄ ²⁻	1.02 x 10 ⁻⁷	6.91				
Arsenic (2)	H ₂ AsO ₄ ⁻	HAsO ₄ ²⁻	8/9.3 x 10 ⁻⁸	7.10/7.03				
Hydrosulfuric	H ₂ S	HS ⁻	1.0 x 10 ⁻⁷ /9.1 x 10 ⁻⁸	7/7.04				
Phosphoric (2)	H ₂ PO ₄ ⁻	HPO ₄ ²⁻	6.23 x 10 ⁻⁸	7.21				
Hypochlorous	HClO	ClO ⁻	3.5/3.0 x 10 ⁻⁸	7.46/7.53				
Hypobromous	HBrO	BrO ⁻	2 x 10 ⁻⁹	8.70				
Hydrocyanic	HCN	CN ⁻	6.17 x 10 ⁻¹⁰	9.21				
Boric (1)	H ₃ BO ₃	H ₂ BO ₃ ⁻	5.8 x 10 ⁻¹⁰	9.23				
Ammonium ion	NH ₄ ⁺	NH ₃	5.6 x 10 ⁻¹⁰	9.25				
Phenol	C ₆ H ₅ OH	C ₆ H ₅ O ⁻	1.6 x 10 ⁻¹⁰	9.80				
Carbonic (2)	HCO ₃ ⁻	CO ₃ ²⁻	4.8 x 10 ⁻¹¹	10.32				
Hypoiodous	HIO	IO ⁻	2 x 10 ⁻¹¹	10.70				
Arsenic (3)	HAsO ₄ ²⁻	AsO ₄ ³⁻	6.0 x 10 ⁻¹⁰ /3.0 x 10 ⁻¹²	9.22/11.53				
Hydrogen peroxide	H ₂ O ₂	HO ₂ ⁻	2.4 x 10 ⁻¹²	11.62				
Ascorbic (2)	HC ₆ H ₆ O ₆ ⁻	C ₆ H ₆ O ₆ ²⁻	1.6 x 10 ⁻¹²	11.80				
Phosphoric (3)	HPO ₄ ²⁻	PO ₄ ³⁻	4.8/2.2 x 10 ⁻¹³	12.32/12.66				
Water	H ₂ O	OH ⁻	1.0 x 10 ⁻¹⁴	14.0				
Group I metal hydroxides (LiOH, NaOH, etc.)			Strong bases completely dissociate in aq solution (Kb > 1, pKb < 1). Conjugate acids (cations) of strong bases are ineffective bases.					
Group II metal hydroxides (Mg(OH) ₂ , Ba(OH) ₂ , etc.)								

* Compiled from Appendix 5 Chem 1A, B, C Lab Manual and Zumdahl 6th Ed. The pKa values for organic acids can be found in Appendix II of Bruice 5th Ed.

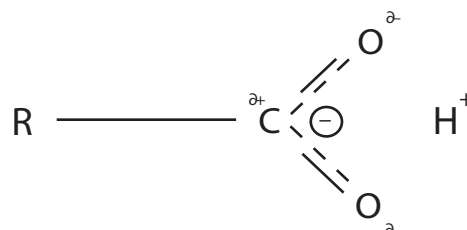
Source: University of California, Santa Barbara.

- Let us start our explanation of what determines the strength of a Carboxylic Acid with a reminder of what an acid looks like.

Two of the Resonance forms of a Carboxylic Acid

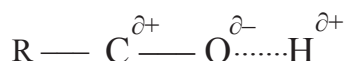


The dashed line indicates the delocalisation of the electron in the acid.

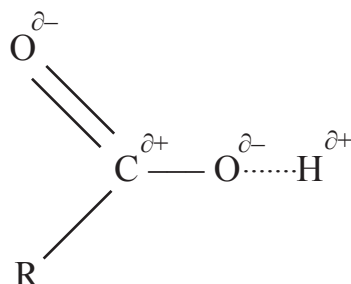


- The strength of an acid (any acid, Carboxylic or otherwise) will be determined by how tightly the dissociable H^+ proton is held onto the molecule. I am therefore going to draw the above molecule in a manner in which this point will be made more (visually) obviously. (Dotted lines indicate bonds that are weakened by the fact that the species at one end of the bond is more electronegative than the species at the other end.)

An Alcohol

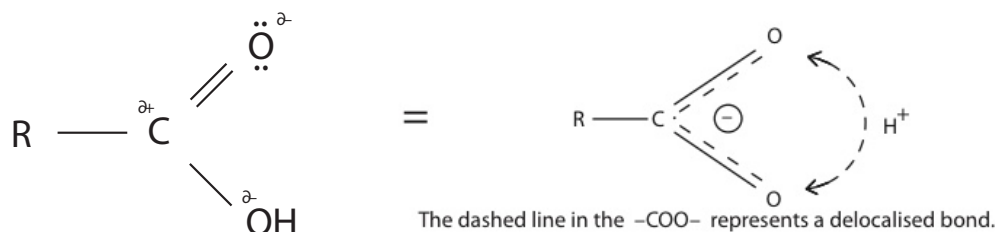


A Carboxylic Acid

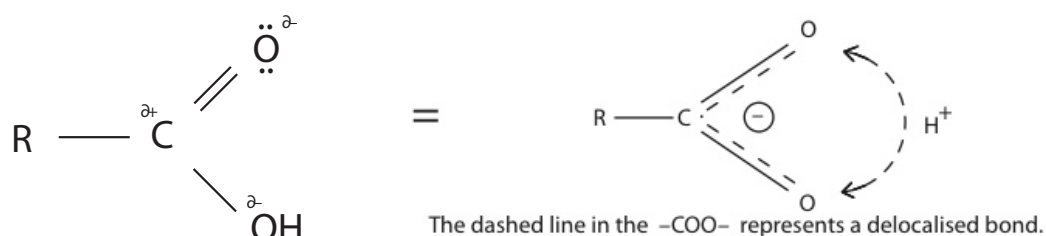


- For the Alcohol and the Acid above to dissociate their protons, in the molecules as I have now drawn them, the proton has to break away from the $O^{\delta-}$ that is holding onto them, and now this is the bit that is important.
- In the Alcohol, the O atom has pulled electron density away from the H atom and where there was previously a full “O–H” bond, that bond has now been weakened by the fact that the electron density has now shifted to the left (towards the O atom) and thus the “O–H” bond has been weakened. The $H^{\delta+}$ atom therefore now has a tiny bit of leeway to break away from the $O^{\delta-}$ atom.
- However if we look at the Acid, the O atom at the end of the double bond has pulled electron density off the C atom which has therefore pulled electron density off the “ $C^{\delta+} - O^{\delta-}$ ” bond, and this has now weakened the bond between the $H^{\delta+}$ and the $C^{\delta-}$ atoms **even further**. This means that the H^+ proton can break away from the Acid much more easily than it can in the Alcohol.
- Protons in Carboxylic Acids are thus more easily dissociated than they are in Alcohols, and this makes Carboxylic Acids more acidic than Alcohols!**
- OK, we can now see that the acidity of an organic molecule is determined by what happens to the electron density on the $O^{\delta-}$ atom that is holding on to the $H^{\delta+}$ proton. What then would happen if we were to make other changes to the electron density on the $C^{\delta-}$ atom?

- In Chapter 21 itself, I said to you that I would like you to think of a Carboxylic Acid (“RCOOH”) in the way that I described it to you last year viz. where the proton (in a sense) flits between the two (Resonance) O atoms.



- The delocalisation of the unhybridised π electrons on the two O atoms and the C atom reduces the $\text{C}^{\delta+}$ nature of the C atom and imparts stability to the little group of 3 atoms (-COO-).



- The reason that I want you to think of a Carboxylic Acid in this way is that if you now concentrate on the “R” (and please remember that “R” can be any legitimate organic configuration), then I can now tell you that
 - Carboxylic Acids [RCOOH or R-COOH or R.C=O(OH)] are weak acids** and their position of dynamic equilibrium lies far to the left of the reaction (i.e. they dissociate only a very small proportion of their protons before dynamic equilibrium is reached)

$$\text{RCOOH} \rightleftharpoons \text{H}^+ + \text{RCOO}^-$$
 where dynamic equilibrium lies **very far** to the left for a Carboxylic Acid
 - but if “R” consists of an **EDG** (Electron Donating Group⁴) then the more electron donating the group, the more electron density there will be on the “ -COO^- ” bit of the Acid, and therefore the more strongly will the proton (H^+) be held and the **weaker** will the Acid be (the more electron donating that “R” is, the more the position of dynamic equilibrium will move to the left)⁵
 - whereas if “R” consists of an **EWG** (Electron Withdrawing Group), then the more will electron density be pulled off the “ -COO^- ” bit of the Acid, and therefore the more easily will the proton (H^+) be dissociated and the more will the position of dynamic equilibrium shift to the right and the smaller will the resulting pK_a and pH be, and the **stronger** will the Acid be.⁶

⁴ The correct label for an EDG species is an “Electron **Density** Donating Group”. No electrons are transferred! The same applies to “Electron **Density** Withdrawing Groups”.

⁵ The **weaker** an Acid, the **larger** will its pK_a and its pH be (and the more basic will it be).

⁶ The **STRONGER** an Acid, the **SMALLER** will its pK_a and pH be.

- **Substituent Halogen atoms increase acid strength!**
- Let's have a look at our earlier table and see whether the facts fit our hypothesis – and, by golly, we can see that the pKa of Ethanoic Acid is 4.76 while that of Chloroethanoic Acid is 2.86 and that of Di-chloroethanoic Acid is right down to 1.29. Eureka! **The facts fit the hypothesis!**

<u>Substance</u>	<u>Acidity</u>	<u>pKa value</u>
Di-chloro ethanoic Acid	Strong acid	1.29
Sulphuric Acid	Strong acid	1.92
Chloroethanoic Acid (this used to be called chloroacetic acid)	Weakish acid	2.86
Methanoic Acid (this used to be called formic acid)	Weak acid	3.75
Benzoic Acid	Weak acid	4.20
Ethanoic Acid (this used to be called acetic acid)	Weak acid	4.76
Butanoic Acid	Weak acid	4.82
2-methylpropanoic Acid	Weak acid	4.85
Propanoic Acid	Weak acid	4.87
tri-methyl ethanoic Acid	Weak acid	5.05
Phenol	Very weak acid	10.00
Water	Neutral	14.00
Methanol	Hardly acidic at all	15.50
Methane	Not acidic	

- OK, let's try it a different way. We know that Alcohols are hardly acidic at all. In fact, you have to add in the H^+ protons from the dissociation of Water itself to bring the pKa of Methanol below "14" and *that* is how Alcohols qualify for the classification of "Hardly acidic at all".
- What in that case can we say about Phenol? Well, if you cast your mind back to Phenol (Chapter 15), you will remember that the electrons in the 'p' orbital of the Oxygen atom in Phenol get locked into the delocalised π ring of the Benzene ring via a negative mesomeric effect; and, because the electron density on the O atom is "locked" into the delocalised π ring, the H^+ proton should dissociate more easily than in an ordinary Alcohol (where there is no delocalisation). If we look at the table of pKa values, we can see that the pKa for Methanol is 15.5 while that for Phenol is only 10.00!
- I will not belabour the point any further because I can tell you that the theory is absolutely justified by the facts that have been established by experiment after experiment. (In fact, the theory had to be developed because the facts are what they are.)

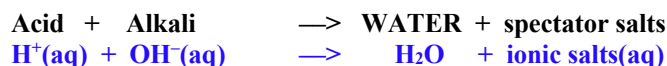
A **I**ncrease in electron density on the $O^{\delta-}$ atom

- It will not surprise you to hear that when electron density is **increased** on the $O^{\delta-}$ atom that holds on to the $H^{\delta+}$ atom, then the $H^{\delta+}$ proton is held more tightly, and fewer H^+ protons are dissociated and thus the molecule becomes less acidic. (Please remember that the lower the concentration of protons, the weaker the acid.)

Propanoic Acid > Ethanoic Acid > Methanoic Acid
and that is exactly what the table says – but it does not work for Butanoic Acid. Why does it not?

- If you remember, right at the beginning of this Chapter I said “There are many factors that affect the ease of dissociation of a proton from a substance, but for ‘A’ Level, the only factors that I shall consider are electronegativity and charge density” – and this is where charge density comes into play. A Butanoic Acid molecule is larger than a Propanoic Acid molecule, therefore the extra electron density that is pushed onto the O^{\ominus} atom that holds on to the H^{\oplus} atom is spread over a larger volume of space and therefore its extra electron density is diminished by the larger volume and it therefore is **not** a stronger acid than Propanoic Acid. In fact, the explanation is a bit more complicated than that, but that is enough for ‘A’ Level purposes.

- Let me remind 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.

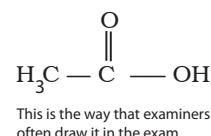
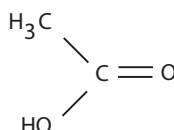
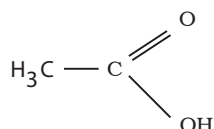


- However, some Acid-Base⁷ reactions do not produce any water, therefore the definition had to be broadened to take this into account, and accordingly, the **Bronsted-Lowry** definition an Acid became
An Acid is a proton donor / A base is a proton acceptor

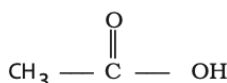
- and the great Gilbert Lewis then broadened the definition still further and said
An Acid is a substance that accepts a pair of electrons / A base is an electron pair donor
- The change in definition did not change any of the reactions themselves. It just meant that a larger ‘set’ of reactions came 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

⁷ An “alkali” is a soluble “base”.

- 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 $\text{H}_3\text{O}^+(\text{aq})$ or $\text{H}^+(\text{aq})$ (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 most of these descriptions, where the “Carboxylic” bit means that the acids are Carbon based species. There are many ways to draw a Carboxylic Acid, and here are three ways for drawing Ethanoic Acid.



- 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.)**

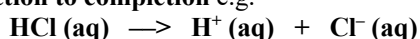


or this could be written as “**R-COOH**”.

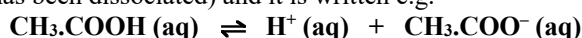
- Functionally a Carboxylic Acid is the same as a non-Carboxylic Acid. The main difference between a non-Carboxylic Acid and a Carboxylic Acid is that **most** Carboxylic Acids are weak acids. Let us therefore look at this aspect of Carboxylic Acids.

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, Sulfuric Acid, Nitric Acid, Hydrobromic Acid, Hydroiodic Acid, Perchloric Acid, and Chloric Acid) so much so that the reaction with water should be written as a **reaction to completion** e.g.

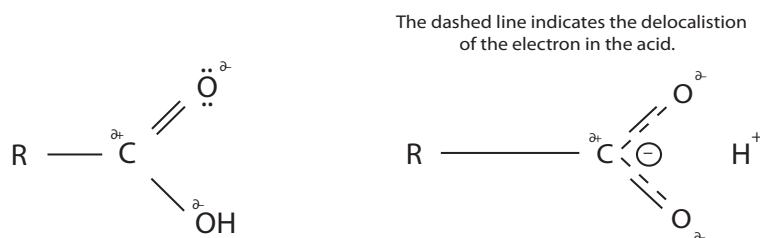


whereas a weak acid is one that is formed as a result of a reversible reaction where the position of dynamic equilibrium lies very far to the left (viz. dynamic equilibrium is reached when only a very small proportion of the available protons has been dissociated) and it is written e.g.



- The way that your understanding of this will be tested in the exams is to ask you about relative strengths of acids.
- i) You could be given the pKa value of different acids, and then asked why they have pKa values of that *relative* magnitude, or
- ii) 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 overleaf).**

Two of the Resonance forms of a Carboxylic Acid



- The greater the electron density that there is in the “ $-\text{CO}^{\delta-}-\text{O}^{\delta-}$ ” area, then the more will the H^+ be attracted to the electron density, and the more tightly will the H^+ be held, **and the harder it will 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. $-\text{C}_n\text{H}_{2n+1}$), whereas there are many species that ‘pull 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).

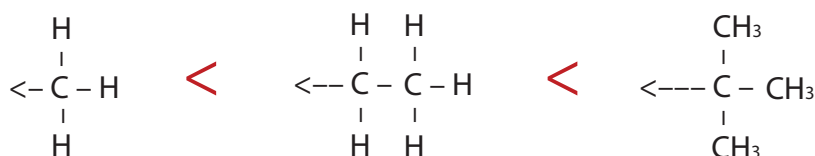
Species that PUSH electron density onto another species

- 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 etc. This feature is commonly expressed as



where “ $<-$ ” stands for “is pushing electron density”, and “ $<$ ” stands for the normal usage of “less than” and “ $-\text{C}_4\text{H}_9$ ” therefore pushes more electron density than “ $-\text{C}_3\text{H}_7$ ”.

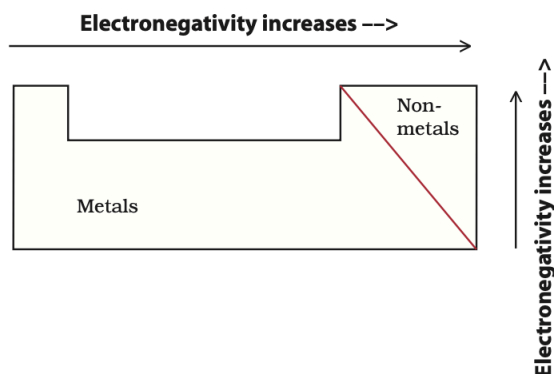
- I drew those species in a straight line, but I could have drawn it differently viz.



- 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 be 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 pK_a value of an acid, the smaller will its pH value be (and the stronger will it be as an acid); the larger the K_a the stronger the acid, but **the smaller the pK_a and the smaller the pH , the STRONGER will the acid be.**

Species that suck electron density off other species

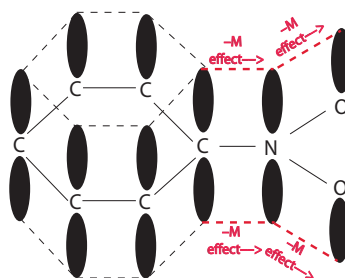
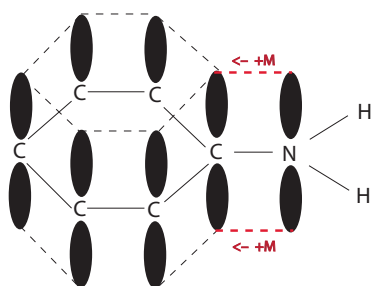
- There is literally a huge number of species that suck electron density off other species, and it is entirely to do with the difference in electronegativity. In a Periodic Table, electronegativity increases
 - across each Period, and
 - up each Group.



- 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, “ $\text{--->CH}_2\text{Cl}$ ” will withdraw less electron density than will “ --->CHCl_2 ”, and in turn it will pull less electron density than “ --->CCl_3 ”. Using the symbols that we used earlier,

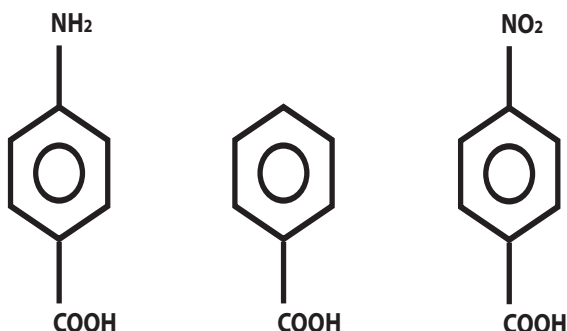
“ $\text{--->CH}_2\text{Cl}$ ” < “ --->CHCl_2 ” < “ --->CCl_3 ” and

“ $\text{--->CH}_2\text{Cl}$ ” < “ $\text{--->CH}_2\text{N}$ ” < “ $\text{--->CH}_2\text{O}$ ” < “ $\text{--->CH}_2\text{F}$ ” 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 Benzene, and it will become very clear. The comparison between $\text{C}_6\text{H}_5.\text{NH}_2$ (Phenylamine/Aniline/) and $\text{C}_6\text{H}_5.\text{NO}_2$ (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 “ $\text{CO}^{\delta-}\text{O}^{\delta-}$ ” 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 sort of question used to be called a “no-brainer” because you did not have to have a brain to work out that

4-nitrobenzoic acid > benzoic acid > 4-aminobenzoic acid
 $\text{pK}_a \approx$ 3.4 4.2 4.8

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

(NB The smaller the pK_a value, the stronger the acid and the smaller the pH value, the stronger the acid.)

- The generic form of an acid is



and the Hydrogen atom *in an acid* is acting like a metal. 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, HA_1 or HA_2 , where A_1 and A_2 can be either single atoms (such as HCl) or a species (such as H_2SO_4 , or $\text{C}_6\text{H}_5\text{COOH}$). 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.

HA_1 is a stronger acid than HA_2 (i.e. it will dissociate more protons) if

- A_1 is more electronegative than A_2 .** I have shown below the bonding pair of electrons as a surrogate for the electron cloud. Because A_1 is more electronegative than A_2 , A_1 has drawn the electron cloud much closer to itself, and this allows H^+ to be dissociated more easily than is the case with HA_2 .



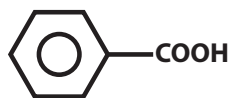
- A_1 is physically larger than A_2 .** Remember the $1/(\text{distance})^2$ effect, and here $d_1 > d_2$ therefore A_1 's hold on its proton is much *less* than A_2 's hold on its proton (because the greater distance diminishes the “hold”) and **strengthens/increases** the acidity.



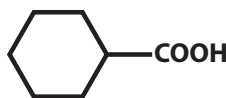
3. **A₁ has resonance stability but A₂ does not.**

C₆H₅.COOH has a pK_a of 4.2 while C₆H₁₁.COOH has a pK_a of 4.8.

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



Benzoic Acid, C₆H₅COOH



Cyclohexane-carboxylic Acid, C₆H₁₁.COOH

NB A stronger acid dissociates more Protons. A weaker acid dissociates fewer Protons.

- There are other rules, but I do not want to make the thing too complicated.
- Overleaf 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

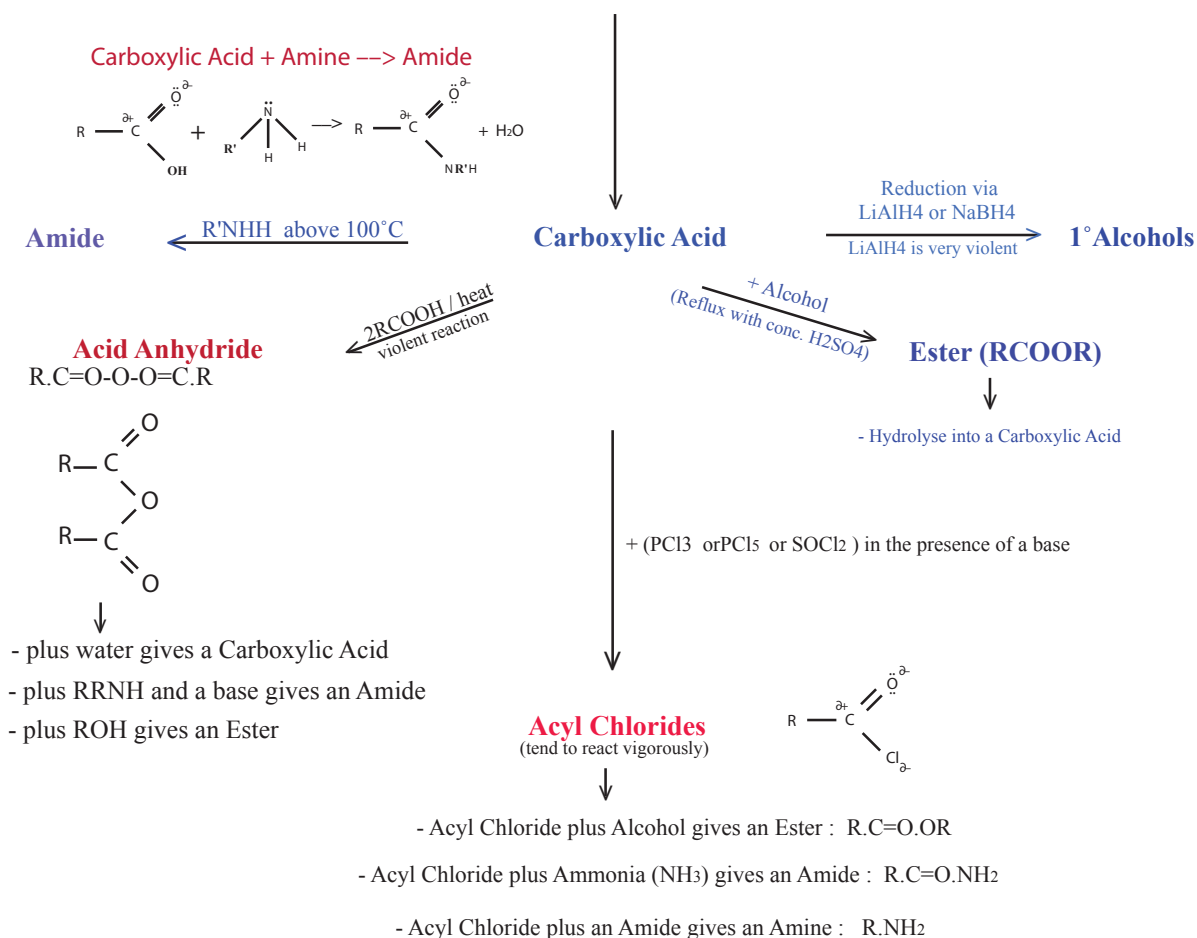
Acyl Chloride plus Water

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 CHI_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.