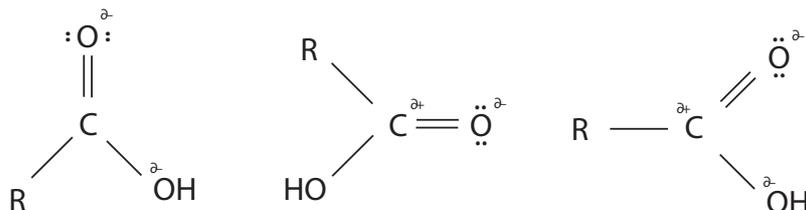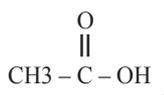# A First Year Blog on Carboxylic Acids
(for the week commencing the 26th of January 2020)
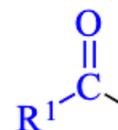
The Structure of Carboxylic Acids

- Before talking about the reactions of Carboxylic Acids, let us look at three ways of drawing a Carboxylic Acid. These are all one and the same molecule.

- In the exams it can be written as $CH3 - C - OH$ (with O double-bonded to C).   This is the "acyl" bit

- As you can see there is a bit of the molecule that resembles an Alcohol (viz. the hydroxy species, "–OH"), and there is a bit that resembles an Alkene (viz. the "C=O" species), and there is the Carbonyl configuration (viz. the " **RR' >C=O** " bit), and it is also the "acyl" species.

One of the important things to remember about Carboxylic Acids is that they are ACIDS
(albeit very weak ones)

- An Acid
  - dissociates Protons (H^+)
  - often reacts with a Base to form WATER and a salt ($H^+ + OH^- \longrightarrow H_2O$) , 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 (thus giving H^+A^-)
  - 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 has been dissociated, whereas
  - a strong Acid is one that when it dissociates its Protons, reaches a position of dynamic equilibrium when a large proportion of its Protons has 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
  - 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, then it will dissociate a Proton to a water molecule to form H_3O^+(aq) just as an Inorganic Acid does, and this will react with some metals to produce H_2(g)/with $CaCO_3$(s) to produce CO_2(g) and H_2O(l)/with an Hydroxide to produce Water plus a salt/etc.

- *Concentration* is the molar concentration in mol/L (Molar or M). This can also be referred to as **molarity**. Molarity is defined as the number of moles of solute dissolved per litre of solution (mol/L = M). A one mol dm^{-3} (1M) solution is one in which exactly 1 mole of solute is dissolved in a total solution volume of exactly 1 L. The concentration may also be expressed in different fractions of the molar concentration such as mmol/L (mM), μmol/L (μM) / etc.

- Both this year and last year, when I was teaching you about Acids, I stressed the fact that the pH of an Acid is a measure of the concentration of H^+ ions in a solution of that Acid. If you use a concentration of 1 mol dm^{-3} of an Acid to calculate its pH value then you will get one answer, but if use a concentration of 0.5/or 0.25/or 0.05/or 0.005/or whatever mol dm^{-3}, then you will get a different pH value **for the very same Acid**. **Please remember that fact as you read on.**
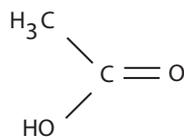

<u>Organic Acids</u>

- When scientists started discovering Acids, they knew nothing whatsoever of all the stuff that I have been telling you. In fact, until the Renaissance, in Europe, the poor women who had the temerity to use their brains to make scientific discoveries were classed as witches and they were either drowned or burnt at the stake. Can you believe that! That just shows you how perverted religious people can become when they forget their primary injunctions viz. (i) to love God and (ii) to love His or Her creation. *(If there is such an entity as "God", then clearly God cannot have a gender.)* In contrast, men who were interested in Chemistry were called "Alchemists" and were not killed but instead were locked in dungeons by Kings/Princes/Dukes to try to make gold out of other substances.[1]

- When we in Europe eventually left the Dark Ages, Acids were originally made by distillation from naturally occurring organic materials such as fruit/milk/etc.

- In your first year I told you that in order to name a Carboxylic Acid and its derivatives, you should always start with the Alkane name for the molecule and then knock off the "-e" at the end of the name, and then add "....-oic Acid". You must start counting from the C atom that contains the Functional Group, i.e. the Carbon atom in the "-COOH" part of the chain **MUST** be counted in as part of the Carbon chain. *[The symbol "R" is used to indicate that this bit of the compound is any* **legitimate** *section of a Carbon molecule.]*

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[1] This not only tells you how cruel and barbaric our ancestors in Europe were, but how **sexist** they were. Strangely enough this was **not** the case in the Islamic Middle East where (until the Muslims lost the plot around the 13th century), knowledge was encouraged by the Qu'ran and valued enormously by Muslims.
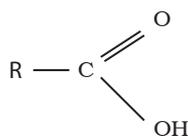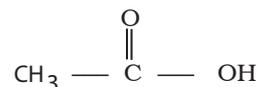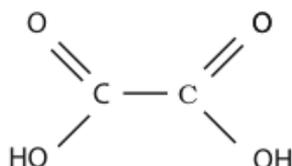
Functional group	e.g. Ethanoic Acid	An examiner might draw it like this

NB This is **NOT** an Alcohol. It is an **ACID**! The single-bonded Hydroxy Group (i.e. the -OH group) attached to the double-bonded C atom in the Carbonyl Group (i.e. the "C=O" group) makes this a Carboxylic Acid.

EthaneDIoic Acid   **EthaneDIoic**
[The "di" is in capitals merely for emphasis!]
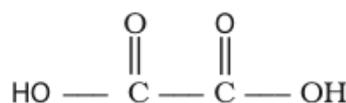
• There was a time when the examiners used to like using Ethanedioic Acid in exams (it used to be called Oxalic Acid) – because it showed that even if students had not actually encountered the compound, nevertheless they could use their brains to work out the structure of the Acid. Any Acid that contains two "–**COOH**" species is called a "–dioic Acid" (e.g. Butanedioic Acid).

The Names of Organic Acids

• A Carboxylic Acid has the form **RCOOH** or **R.COOH** or **R–COOH** or **R.C=O(OH)**, but please remember that a Lewis Base is a lone pair donor, therefore anything that donates a lone of electrons to an organic species will make an organic species into an organic Acid (but I am not going to talk about organic Sulphonic Acids here).

• We no longer use the olden names for organic Acids such as

Old Name	Modern Name	Structural Formula
Formic Acid (from the Latin word for 'ant')	Methanoic Acid	H.**COOH**
Acetic Acid	Ethanoic Acid	CH_3.**COOH**
Propionic Acid	Propanoic Acid	C_2H_5.**COOH**
Butyric Acid	Butanoic Acid	C_3H_7. **COOH**
and so on.		

• Please remember to start counting from the C in "–**COOH**" and then identify all the different species that are attached to the C chain and where they are attached.

• We have not talked about Arenes (i.e. Benzene and its sister delocalised π ring compounds) for some time so please do not forget that the "R" in "RCOOH" can be an aryl species e.g. Benzoic Acid is C_6H_5.COOH.

- Right, to show that you have not forgotten what I told you elsewhere, could you now draw 4-methylbenzoic Acid and the three o- / m- / and p-hydroxybenzoic Acids[2] (or as I prefer to call them 2-hydroxybenzoic Acid / 3-hydroxybenzoic Acid / and 4-hydroxybenzoic Acid). I am not a big fan of the labels *"ortho" / "meta" / and "para"*. The days when people learnt Greek at school are long gone.

The Reactions of Organic Acids

- The sub-heading above is misleading because an organic Acid *is just an Acid*. It must behave just like an Acid. The sub-heading therefore requires you to concentrate on the word "**organic**" because we are now going to look at things that organic Acids do. On the whole, Carboxylic Acids act like ordinary Acids and are constrained by the rules that I set out on page 1.

- Unlike its sister Carbonyl compounds, Carboxylic Acids tend **not** to undergo nucleophilic reactions. Please remember that nucleophiles are entities that possess a negative charge ("–") or a "∂–"area, or a lone/unbonded pair of electrons; and, in a normal carbonyl compound, the electron density has been pulled so much onto the O atom that the $C^{\partial+}$ atom has been left totally exposed to a nucleophilic attack (as shown below[3]).

Carbonyl Compounds

This ∂+ flank is left exposed to an attack by a nucleophile —>
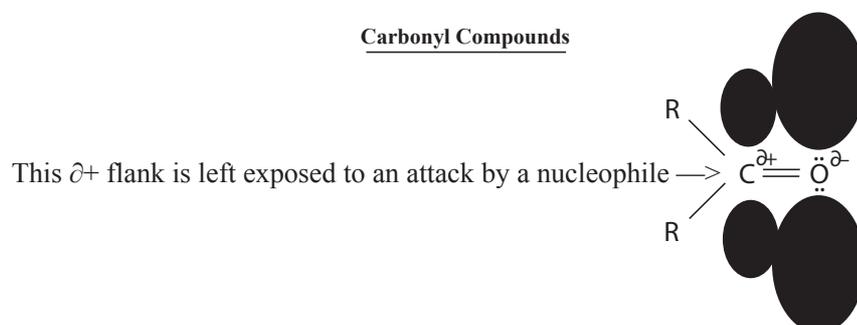
- As we have already seen, the derivatives of Carboxylic Acids (such as Aldehyes/Ketones/Nitriles/ etc) are subject to nucleophilic attack on the $C^{\partial+}$ atom, but a **Carboxylic Acid itself** is **NOT** susceptible to a nucleophilic attack because the delocalisation of the unhybridised π electrons on the two O atoms **and the C atom** reduces the $C^{\partial+}$ nature of the C atom and imparts stability to the little group of 3 atoms (–COO–).

The dashed line in the –COO– represents a delocalised bond.
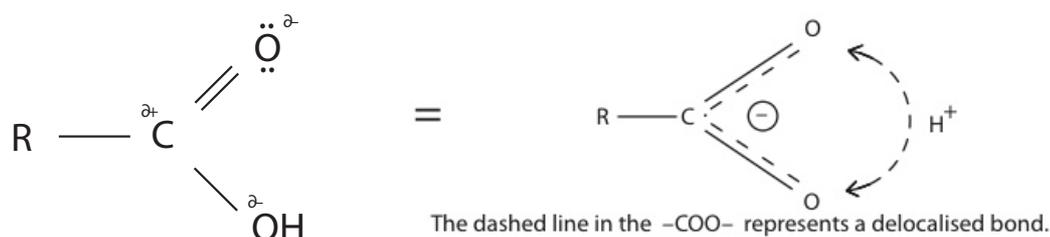
- The O atoms are certainly more electronegative than the C atom, but this is offset by the negative nature of the delocalised π ring and **the $C^{\partial+}$ is thus NOT susceptible to a nucleophilic attack.** Other Carbonyl compounds are subject to nucleophilic attack, but Carboxylic Acids are subject to attack by electrophiles (that are attracted to the delocalised π electrons).

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[2] The mnemonic is OMP or "Oh Mein Pappa".
[3] I do not know how to make Adobe Illustrator shade the pulling of electron density off the $C^{\partial+}$ by $O^{\partial-}$.

Carboxylic Acids are weak Acids (with pH values in the region of 3-5)

- 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 dashed line in the –COO– represents a delocalised bond.
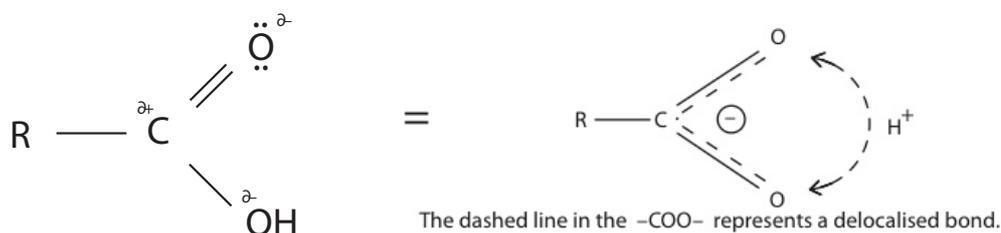
- The reason that I want you to think of a Carboxylic Acid in this way is that if you now concentrate on the "R" (and please remember that "R" can be any legitimate organic configuration), then I can now tell you that

  - **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)
    $$RCOOH \rightleftharpoons H^+ + RCOO^-$$
    where dynamic equilibrium lies **very far** to the left for a Carboxylic Acid

  - but **if "R" consists of an EDG** (Electron Donating Group[4]) 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]

- OK, I have here (I hope) done a number of things. For the last few weeks, every time that I have seen you, we have talked about Organic Chemistry – and much as I love Organic Chemistry, I must not neglect the Inorganic things that we must learn at 'A' Level. In the next bit I have therefore melded the two studies together in order to remind you of (i) dynamic equilibria and (ii) the mathematical function that 'logs' have in the analysis of the strengths of Acids and Bases.
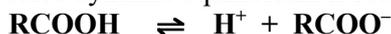
- When a **reversible** reaction $\qquad aA + bB \rightleftharpoons cC + dD$
  reaches dynamic equilibrium **at a given temperature**,[7] then there is a number/a Constant, K_c that expresses the following ratio

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[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.
[7] .... and please remember that the reaction MUST have reached dynamic equilibrium, and that some reactions do this quickly while other reactions take a long time (a week/a month/a year/5 billion years/whatever) to reach this point. Please do not confuse the position of dynamic equilibrium with the RATE at which equilibrium is reached. **"How far" is not the same as "How fast".**

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \qquad \text{at equilibrium at a given temperature[8]}$$

NB The square brackets indicate the "concentration" of the relevant product or reactant raised to its stoichiometric number, and for an Acid we can multiply K_c by the concentration of Water to obtain K_a :   **K_c x (the concentration of H^+ ions in Water[9]) = K_a** .

- For an Acid, the further to the right that the position of dynamic equilibrium lies, the larger will be the concentration of H^+ cations (Protons) and by definition the larger will the concentration of salt anions be (e.g. Cl^- ions from HCl, or SO_4^{2-} ions from H_2SO_4), therefore the larger will K_a be.

- For pure Water, K_c x (concentration of H^+ ions in Water) = K_a = $[H^+].[OH^-]$, and the concentration of H^+ cations (Protons) in pure water = the concentration of OH^- ions viz.

$$[H^+] = [OH^-] = 1 \times 10^{-7} = 10^{-7} \qquad \textbf{at 298K}$$

- The 'p' of anything is "$-\log_{10}$" of that thing, therefore the pK_a of pure Water is given by K_a = $[10^{-7}].[10^{-7}]$ = $[10^{-14}]$, therefore the pK_a of pure Water = $-\log_{10}(10^{-14})$ = **+14**
(Please ignore any statements to the effect that the pK_a of pure Water is 15.7. There is a dispute going about that claim in the world of Chemistry.)

- As we have seen, the term "pH" = $-\log_{10}$(the concentration of H^+ ions in that substance), therefore from the above, the pH of pure Water = $-\log_{10}(10^{-7})$ = **+7**   (at 298K).

- For pure Water the
$[H^+]$ = 1×10^{-7} = 10^{-7}
K_a = 10^{-14}
pK_a =   14   , and
pH   =   **7** (you learnt this last fact in your very first year of Chemistry when you were 12 years of age).

- If you are at all unsure about what I have just said, then please read that again. You must be able to distinguish between

  $[H^+]$ the concentration of H^+ ions in a substance, and
  K_a   the constant that gives the relationship between the concentration of *products* to the power of their stoichiometric ratios divided by the concentration of the *reactants* to their stoichiometric ratios, and
  pK_a $-\log_{10}(K_a)$, and
  pH $-\log_{10}([H^+])$.

- For the moment I do not want you to do anything more than glance through the table below. (CLAS just stands for the University of Santa Barbara's "Campus Learning Assistance Services".)

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[8] The symbol " [X] " means "the **Concentration** of the substance X", where $C = N \div V$, where "N" is the number of moles and "V" is the volume in cubic decimetres (dm^3), and C is thus expressed in mol dm^{-3}.
[9] = 55.555555555 recurring = $55.\dot{5}$.

Table of Acids with Ka and pKa Values* **CLAS**

Acid	HA	A⁻	Ka	pKa	Acid Strength	Conjugate Base Strength
Hydroiodic	HI	I^-				
Hydrobromic	HBr	Br^-				
Perchloric	$HClO_4$	ClO_4^-	Strong acids completely dissociate in aq solution			
Hydrochloric	HCl	Cl^-	($Ka > 1$, $pKa < 1$).			
Chloric	$HClO_3$	ClO_3^-	Conjugate bases of strong acids are ineffective bases.			
Sulfuric (1)	H_2SO_4	HSO_4^-				
Nitric	HNO_3	NO_3^-				
Hydronium ion	H_3O^+	H_2O	1	0.0		
Iodic	HIO_3	IO_3^-	1.6×10^{-1}	0.80		
Oxalic (1)	$H_2C_2O_4$	$HC_2O_4^-$	5.9×10^{-2}	1.23		
Sulfurous (1)	H_2SO_3	HSO_3^-	1.54×10^{-2}	1.81		
Sulfuric (2)	HSO_4^-	SO_4^{2-}	1.2×10^{-2}	1.92		
Chlorous	$HClO_2$	ClO_2^-	1.1×10^{-2}	1.96		
Phosphoric (1)	H_3PO_4	$H_2PO_4^-$	7.52×10^{-3}	2.12		
Arsenic (1)	H_3AsO_4	$H_2AsO_4^-$	5.0×10^{-3}	2.30		
Chloroacetic	$CH_2ClCOOH$	CH_2ClCOO^-	1.4×10^{-3}	2.85		
Citric (1)	$H_3C_6H_5O_7$	$H_2C_6H_5O_7^-$	8.4×10^{-4}	3.08		
Hydrofluoric	HF	F^-	7.2×10^{-4}	3.14		
Nitrous	HNO_2	NO_2^-	4.0×10^{-4}	3.39		
Formic	HCOOH	$HCOO^-$	1.77×10^{-4}	3.75		
Lactic	$HCH_3H_5O_3$	$CH_3H_5O_3^-$	1.38×10^{-4}	3.86		
Ascorbic (1)	$H_2C_6H_6O_6$	$HC_6H_6O_6^-$	7.9×10^{-5}	4.10		
Benzoic	C_6H_5COOH	$C_6H_5COO^-$	6.46×10^{-5}	4.19		
Oxalic (2)	$HC_2O_4^-$	$C_2O_4^{2-}$	6.4×10^{-5}	4.19		
Hydrazoic	HN_3	N_3^-	1.9×10^{-5}	4.72		
Citric (2)	$H_2C_6H_5O_7^-$	$HC_6H_5O_7^{2-}$	1.8×10^{-5}	4.74		
Acetic	CH_3COOH	CH_3COO^-	1.76×10^{-5}	4.75		
Propionic	CH_3CH_2COOH	$CH_3CH_2COO^-$	1.34×10^{-5}	4.87		
Pyridinium ion	$C_5H_4NH^+$	C_5H_4N	5.6×10^{-6}	5.25		
Citric (3)	$HC_6H_5O_7^{2-}$	$C_6H_5O_7^{3-}$	4.0×10^{-6}	5.40		
Carbonic (1)	H_2CO_3	HCO_3^-	4.3×10^{-7}	6.37		
Sulfurous (2)	HSO_4^-	SO_4^{2-}	1.02×10^{-7}	6.91		
Arsenic (2)	$H_2AsO_4^-$	$HAsO_4^{2-}$	$8/9.3 \times 10^{-8}$	7.10/7.03		
Hydrosulfuric	H_2S	HS^-	$1.0 \times 10^{-7}/9.1 \times 10^{-8}$	7/7.04		
Phosphoric (2)	$H_2PO_4^-$	HPO_4^{2-}	6.23×10^{-8}	7.21		
Hypochlorous	HClO	ClO^-	$3.5/3.0 \times 10^{-8}$	7.46/7.53		
Hypobromous	HBrO	BrO^-	2×10^{-9}	8.70		
Hydrocyanic	HCN	CN^-	6.17×10^{-10}	9.21		
Boric (1)	H_3BO_3	$H_2BO_3^-$	5.8×10^{-10}	9.23		
Ammonium ion	NH_4^+	NH_3	5.6×10^{-10}	9.25		
Phenol	C_6H_5OH	$C_6H_5O^-$	1.6×10^{-10}	9.80		
Carbonic (2)	HCO_3^-	CO_3^{2-}	4.8×10^{-11}	10.32		
Hypoiodous	HIO	IO^-	2×10^{-11}	10.70		
Arsenic (3)	$HAsO_4^{2-}$	AsO_4^{3-}	$6.0 \times 10^{-10}/3.0 \times 10^{-12}$	9.22/11.53		
Hydrogen peroxide	H_2O_2	HO_2^-	2.4×10^{-12}	11.62		
Ascorbic (2)	$HC_6H_6O_6^-$	$C_6H_6O_6^{2-}$	1.6×10^{-12}	11.80		
Phosphoric (3)	HPO_4^{2-}	PO_4^{3-}	$4.8/2.2 \times 10^{-13}$	12.32/12.66		
Water	H_2O	OH^-	1.0×10^{-14}	14.0		
Group I metal hydroxides (LiOH, NaOH, etc.)			Strong bases completely dissociate in aq solution			
Group II metal hydroxides (Mg(OH)₂, Ba(OH)₂, etc.)			($Kb > 1$, $pKb < 1$). Conjugate acids (cations) of strong bases are ineffective bases.			

* 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.

Name of the Acid	Structural Formula	pKa (approximate)

Please remember that the **smaller** the pKa is, the **STRONGER** the Acid will be.

Halogeno-Carboxylic Acids

Trichloroethanoic Acid	$CCl_3.COOH$	0.65
Dichloroethanoic Acid	$CHCl_2.COOH$	1.29
Fluoroethanoic Acid	$CH_2F.COOH$	2.66
Chloroethanoic Acid	$CH_2Cl.COOH$	2.86
Bromoethanoic Acid	$CH_2Br.COOH$	2.90
Iodoethanoic Acid	$CH_2I.COOH$	3.17

Straight Carboxylic Acids (old-fashioned name in brackets)

Methanoic Acid (Formic Acid)	$H.COOH$	3.75
Ethanoic Acid (Acetic Acid)	$CH_3.COOH$	4.76
Propanoic Acid (Proprionic Acid)	$C_2H_5.COOH$	4.87
Butanoic Acid (Butyric Acid)	$C_3H_7.COOH$	4.82 (an anomalous pKa)
Pentanoic Acid (Valeric Acid)	$C_4H_9.COOH$	5.01
Hexanoic Acid	$C_5H_{11}.COOH$	4.88 (another anomaly)
Heptanoic Acid	$C_6H_{13}.COOH$	4.82 (another anomaly)
Phenol	$C_6H_5.COOH$	10.0

The pKa of pure Water at 298K is 14.0. Please ignore any claims to the contrary.

Alcohols

The following substances are **Alcohols**. *They are hardly acidic at all*, but they **will** dissociate one Proton per molecule.)

Methanol	$CH_3.OH$	15.5
Ethanol	$C_2H_5.OH$	16.0
Propanol	$C_3H_7.OH$	17.1

The Protons dissociated by Alcohol **attack metals** and generate $H_2(g)$. **That is precisely why petrols that contain Methanol or Ethanol damage the metals in car engines.** *Methanol is used as an additive only in racing cars, but Ethanol is routinely included in standard petrols in many countries.*

NB All Alcohols are harmful/injurious to the health of human beings. It is thus somewhat surprising that human beings consume Alcohols in such vast quantities. *(Human beings are rather strange creatures.)*

- In an earlier Blog 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 $O^{\partial -}$ atom that holds on to the $H^{\partial +}$ 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.

- These are the reactions that will take you into and out of a Carboxylic Acid.

NB I have written Blogs on Benzene and other Arenes, therefore I have not made any reference to them in the Information Tree on page 1.