

Year 2, Organic Chemistry, Chapter 21:

Carboxylic Acids

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

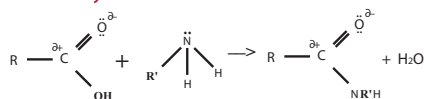
Acid Anhydride plus Water

THE MINOR ROUTES

Tollen's/Fehling's/Benedict's also oxidise Aldehydes into Carboxylic Acids

The Triiodomethane reaction with a methyl Carbonyl compound will produce a Carboxylic Acid and CHI_3

Carboxylic Acid + Amine \rightarrow Amide



[cf. chemguide](#)

Amide

$\xleftarrow{R'NH_2 \text{ above } 100^\circ C}$

Carboxylic Acid

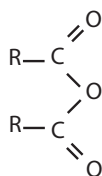
Reduction via
 $LiAlH_4$ or $NaBH_4$

$LiAlH_4$ is very violent

1° Alcohols

[cf. Khan Academy](#)

Acid Anhydride



- plus water gives a Carboxylic Acid
- plus $RR'NH$ and a base gives an Amide
- plus ROH gives an Ester

$\xleftarrow{2RCOOH / \text{heat}}$
violent reaction

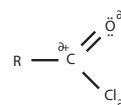
+ Alcohol
(Reflux with conc. H_2SO_4)

Ester ($RCOOR$)

- Hydrolyse into a Carboxylic Acid

+ (PCl_3 or PCl_5 or $SOCl_2$) in the presence of a base

Acyl Chlorides
(tend to react vigorously)



[cf. chemguide](#)

- Acyl Chloride plus cold Water gives an Acid : $R.C=O(OH)$ in a violent reaction

- Acyl Chloride plus Alcohol gives an Ester : $R.C=O.OR$

- Acyl Chloride plus Ammonia (NH_3) gives an Amide : $R.C=O.NH_2$

- Acyl Chloride plus an Amine gives an Amine : $R.NH_2$

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 can be 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.

'A' LEVEL REACTION EQUATIONS FOR CARBOXYLIC ACIDS

(Modestly simplified equations. Create your own equations for YOUR Exam Board. Please use in conjunction with my info tree on Carboxylic Acids.)

R.COOH = Carboxylic Acid / R.C=O(H) = Aldehyde / R.C=O(R') = Ketone / R.C=O(Cl) = Acyl Chloride / R.C=O(O-O=C.R') = Acid Anhydride / R.CH₂OH = Alcohol.

NB A **Nitrile** = R.C≡N / An **Amide** = R.C=O(NH₂) / An **Amine** = R.NH₂.

“Reflux” indicates that the reaction takes a long time and therefore needs to be speeded up/or that it requires a considerable amount of energy to take place.

A precipitate is shown as (s).

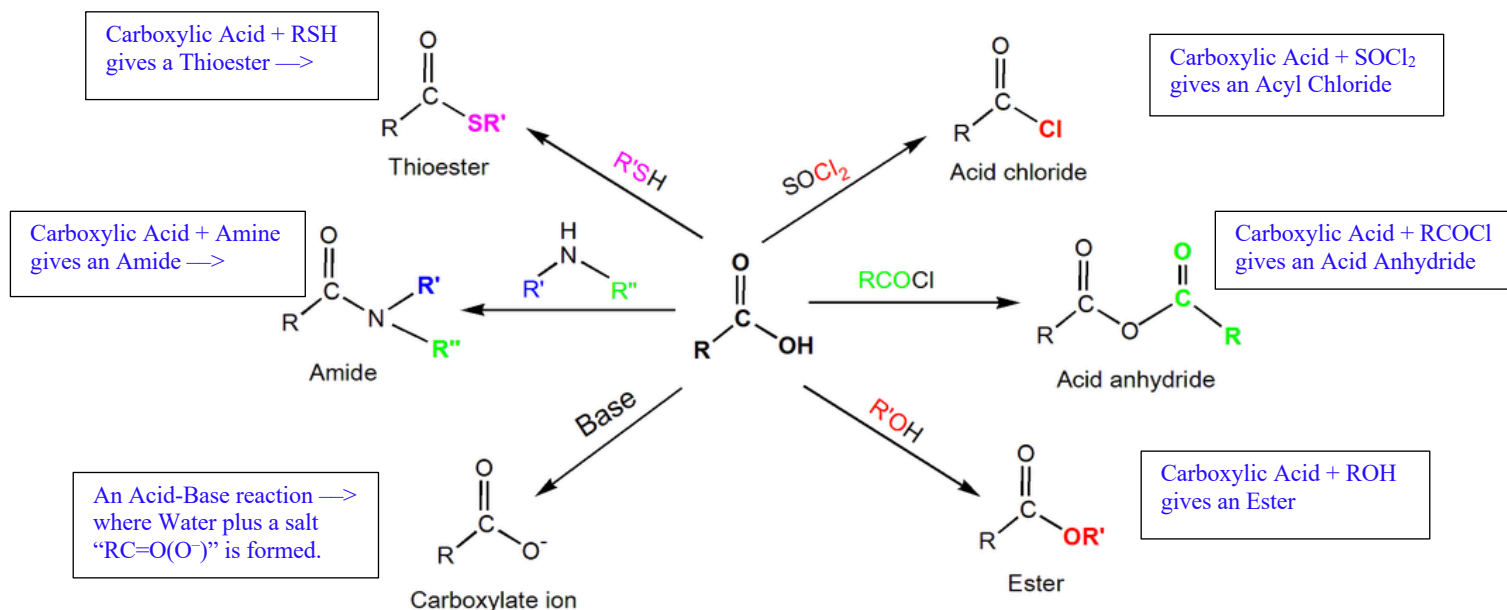
A) Routes INTO a Carboxylic Acid (the reactions of Carboxylic acids as ordinary acids are not shown here)

<u>FROM</u>	<u>REACTION CONDITIONS</u>	<u>REACTION EQUATION</u> (phases/states not always known therefore not included / non-organic products not always shown)	<u>Comment</u>
- Ketones do not oxidise under gentle oxidation (nor do 3° Alcohols)			
- 1° Alcohol	conc. H ₂ SO ₄ / Cr ₂ O ₇ ²⁻	R.CH ₂ OH + 2[O] → R.COOH + Water	Orange to green
- 2° Alcohols oxidise into Ketones but NOT into Carboxylic Acids (other than with aggressive oxidising agents such as MnO ₄ ⁻).			
- 3° Alcohols do not oxidise with gentle oxidising agents.			
- Aldehydes	conc. H ₂ SO ₄ / Cr ₂ O ₇ ²⁻ /heat	R.C=O(H) + [O] → R.COOH	
- Aldehydes	Tollen's ([Ag(NH ₃) ₂] ⁺)	R.C=O(H) + [Ag(NH ₃) ₂] ⁺ [NO ₃] ⁻ → R.COOH + Ag(s) + NH ₃ (g)	Silver ppt
- Aldehydes	Fehling's (Cu ²⁺ /tartarate/OH ⁻ /in situ)	R.C=O(H) + Cu ²⁺ + OH ⁻ → R.COOH + Cu ¹⁺	Blue to coppery-red
- Aldehydes	Benedict's (Cu ²⁺)	R.C=O(H) + Cu ²⁺ + OH ⁻ → R.COOH + Cu ¹⁺	Blue to coppery-red
- CH ₃ .C=O(R)	Iodoform test for Ketones (+I ₂ /OH ⁻)	CH ₃ .C=O(R) + 3I ₂ + 4OH ⁻ → H.COOH + CHI ₃ (s)	Hydrolysis
If Cl ₂ were used instead of I ₂ , then Chloroform (CHCl ₃) would be obtained instead of Iodoform (CHI ₃).			
- Nitriles	dilute H ⁺ or dilute OH ⁻ /heat	RC≡N + 2H ₂ O(l) + HCl(aq) → R.COOH + NH ₄ Cl(g) (if NH ₃ if OH ⁻ is used)	
- Acyl Chloride	+ H ₂ O/pyridine as solvent	R.C=O(Cl) + H ₂ O(l) → R.COOH + HCl	very violent reaction
- Acid Anhydride	+ H ₂ O/pyridine as solvent	(R.C=O) ₂ O + H ₂ O(l) → 2 lots of R.COOH	very violent reaction

B) Routes OUT OF a Carboxylic Acid

<u>TO</u>	<u>REACTION CONDITIONS</u>	<u>REACTION EQUATION</u> (phases/states not always known therefore not included / non-organic products not always shown)
- 1° Alcohol	Reduce with NaBH ₄ or LiAlH ₄	R.COOH + 4H ⁺ + 4e ⁻ → R.CH ₂ OH
- Ester	+ Alcohol (conc. H ₂ SO ₄ as a catalyst/heat)	R.COOH + R'.CH ₂ OH → R.C=O(O.R') The R' comes from the Alcohol
- Amide	+ R'.NHH/heat	R.COOH + R'.NHH → R.C=O(R'.NHH)
- Acyl Chloride	PCl ₅ / OH ⁻	R.COOH + PCl ₅ (s) → R.C=O(Cl) + POCl ₃ (l) + HCl(g)
- Acid Anhydride	H ⁺ / heat	2(R.COOH) → R.C=O-O-O=C.R + water

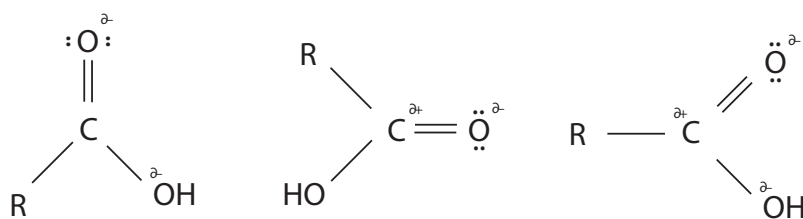
- The Khan Academy at <https://www.khanacademy.org/test-prep/mcat/chemical-processes/carboxylic-Acids/a/carboxylic-Acid-reactions-overview> talks about the following reactions of Carboxylic Acids. (“Thio” indicates an S atom.)



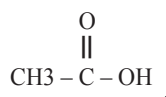
Please take careful note of the names and structures of the substances that are formed in each reaction.

A) The Structure of Carboxylic Acids

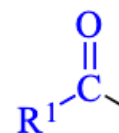
- Before talking about the reactions of Carboxylic Acids, let us look at three ways of drawing a Carboxylic Acid. These are all one and the same molecule.



- In the exams it can be written as



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.

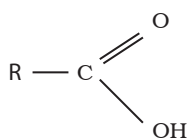
B) One of the important things to remember about Carboxylic Acids is that they are ACIDS
(albeit very weak ones)

- An Acid
 - dissociates Protons (H^+)
 - often reacts with a Base to form WATER and a salt ($H^+ + OH^- \rightarrow H_2O$), 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), $\mu mol/L$ (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.**

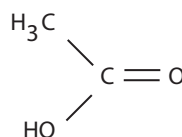
C) Organic Acids

- 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.]*

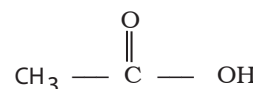
Functional group



e.g. Ethanoic Acid



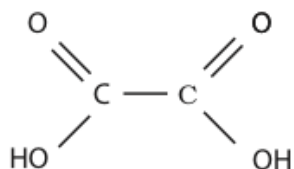
An examiner might draw it like this



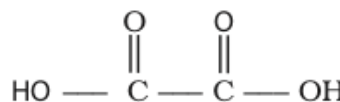
NB This is **NOT** an Alcohol. It is an **ACID**! The single-bonded Hydroxy Group (i.e. the -OH group) attached to the double-bonded C atom in the Carbonyl Group (i.e. the “C=O” group) makes this a Carboxylic Acid.

EthaneDioic Acid

[The “di” is in capitals merely for emphasis!]



EthaneDioic



- 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).

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.

D) 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

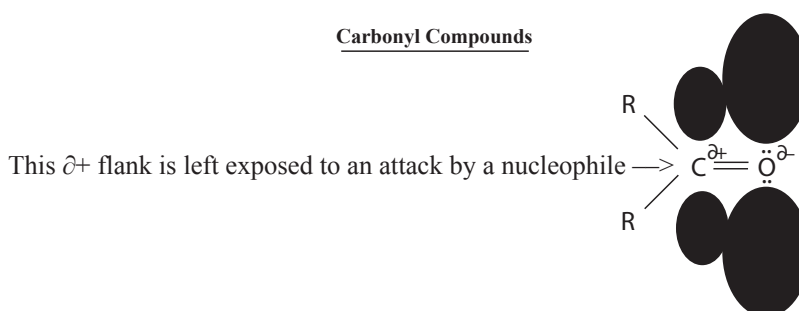
Old Name	Modern Name	Structural Formula
Formic Acid (from the Latin word for 'ant')	Methanoic Acid	H.COOH
Acetic Acid	Ethanoic Acid	CH ₃ .COOH
Propionic Acid	Propanoic Acid	C ₂ H ₅ .COOH
Butyric Acid	Butanoic Acid	C ₃ H ₇ .COOH
and so on.		

- 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 Chapters so please do not forget that the “R” in “RCOOH” can be an aryl species e.g. Benzoic Acid is C₆H₅.COOH.
- Right, to show that you have not forgotten what I told you in the first 15 Chapters, could you now draw 4-methylbenzoic Acid and the three o- / m- / and p-hydroxybenzoic Acids² (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”.*

E) 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 of this Chapter.
- 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 “ δ^- ” 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 ^{δ^+} atom has been left totally exposed to a nucleophilic attack (as shown below³).

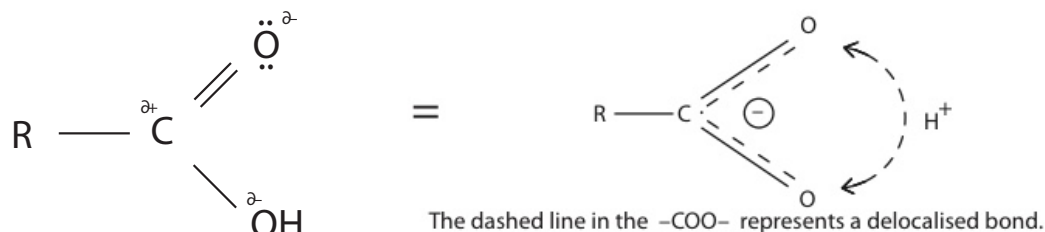
Carbonyl Compounds



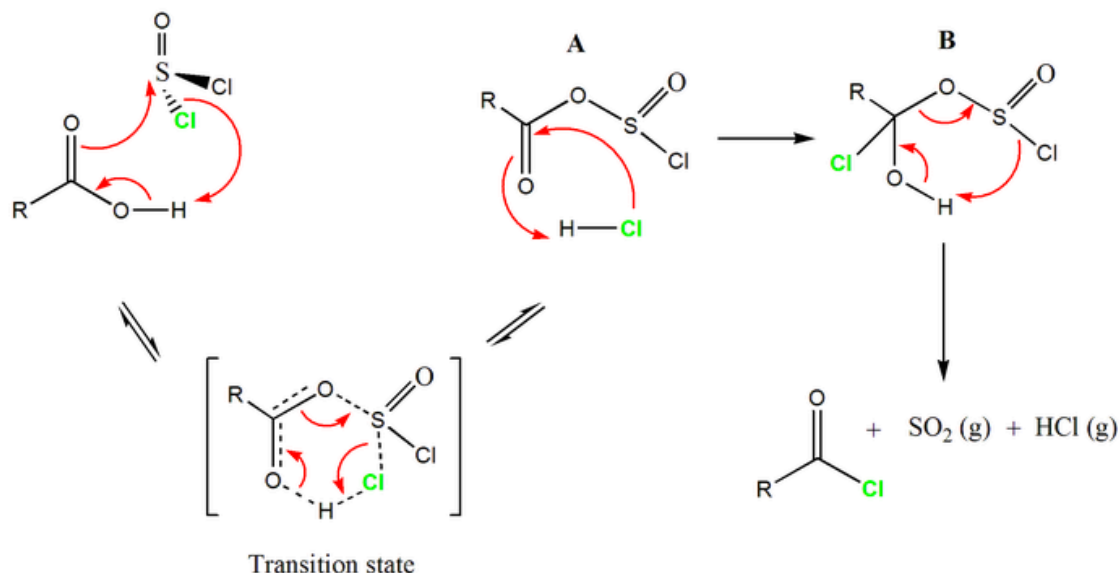
² The mnemonic is OMP or “Oh Mein Pappa”.

³ I do not know how to make Adobe Illustrator shade the pulling of electron density off the C ^{δ^+} by O ^{δ^-} .

- As we have already seen in earlier Chapters, the derivatives of Carboxylic Acids (such as Aldehydes/Ketones/Nitriles/etc) are subject to nucleophilic attack on the $C^{\delta+}$ 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 $C^{\delta+}$ nature of the C atom and imparts stability to the little group of 3 atoms ($-\text{COO}-$).



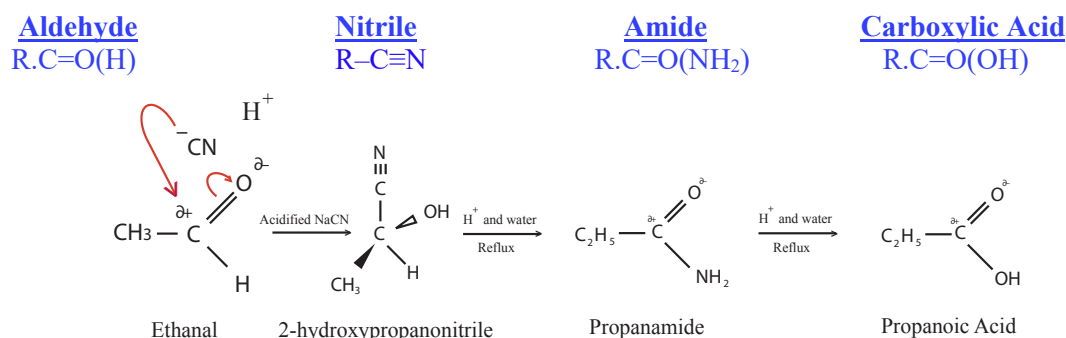
- The O atoms are certainly more electronegative than the C atom, but this is offset by the negative nature of the delocalised π ring and **the $C^{\delta+}$ is thus NOT susceptible to a nucleophilic attack**. Other Carbonyl compounds are subject to nucleophilic attack, but Carboxylic Acids are subject to attack by electrophiles (that are attracted to the delocalised π electrons).
- You can see this in the attack of a Carboxylic Acid by SOCl_2 , where the “S” atom has been severely denuded of electron density by the O atom and the two Cl atoms. $S^{\delta+\delta+\delta+}$ is an **electrophile** (not a nucleophile) and it is attracted to the area of high electron density in the delocalised π ring of the little group of 3 atoms ($-\text{COO}-$). **The initiating movement is thus the electrophilic attack of the $S^{\delta+}$ atom on the delocalised π ring** and you can see this below. In the diagram below, Mr Khan has not shown the S atom as $S^{\delta+}$ – **but it is $S^{\delta+}$** . At this stage, it is only the first diagram that I want you to look at to see that an $S^{\delta+}$ **electrophile** is attacking the Carboxylic Acid. (NB The arrows do not tell you who is attacking what. They tell you about the movement of electrons.)



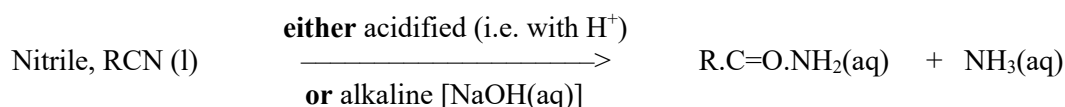
Source: <https://www.khanacademy.org/test-prep/mcat/chemical-processes/carboxylic-Acids/a/carboxylic-Acid-reactions-overview>

F) The Hydrolysis of a Nitrile to a Carboxylic Acid

- The reaction can be effected either through Acid hydrolysis or through Alkaline hydrolysis. Acid hydrolysis is described below.

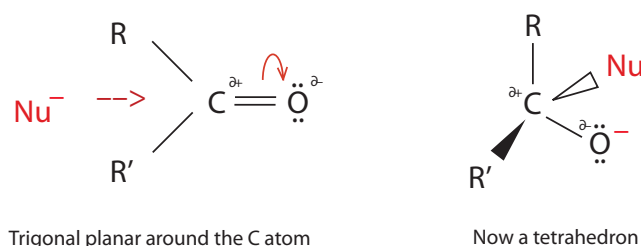


- The first step (Aldehyde to Nitrile) can be effected using HCN, but Hydrogen Cyanide, is a **dangerous substance** and instead of using HCN, it is customary to use a solution of sodium or potassium cyanide in water to which some sulphuric Acid has been added.
- I have mentioned a number of times so far that HCN will react with an Aldehyde or with a Ketone in a complicated set of reactions to form a Nitrile ($R-C\equiv N$)⁴. Chapter 19 contains the explanation of the reaction shown below, but the equation for the reaction of the Nitrile ($R-C\equiv N$) to the Amide $R.C=O(NH_2)$ is as follows



where “C=O” stands for “C double-bond O”. The Alkaline reaction would give $R.C=O.NH_4(aq)$.

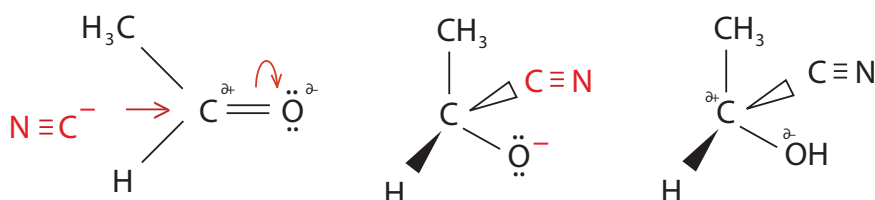
- Technically, the movement of electrons should be shown by curly arrows, but on this occasion I have drawn it below with a straight arrow to show the spearhead of the attack. The Nu^- attacks the $C^{\delta+}$ atom **in the Aldehyde or the Ketone**, and a nucleophilic addition reaction takes place in which the “C=O” double bond breaks heterolytically (and the C atom is then attached to four species instead of three).



- The negative charge that was on the attacking nucleophile is now on the $O^{\delta-}$ atom, and the positively charged companion of the nucleophile is still hovering somewhere in the vicinity. In this part of the reaction, it has played no part.
- With HCN, the H atom in HCN breaks away as a Proton from the HCN ($HCN \rightarrow H^+ + CN^-$), and thereby leaves its electron on the C atom to which it was attached thus leaving the “ $C\equiv N$ ” species with a lone pair of electrons, and thus **the negative charge is on the C atom**.

⁴ Albeit with the addition of one C atom to the number of C atoms that existed in the chain prior to that.

- In the middle species below, the H^+ (from the HCN) will be attracted to the O^- species in the Carbonyl species (here an Aldehyde) and bond with it. The double bond in the “ $\text{C}=\text{O}$ ” has broken heterolytically and the negative charge is therefore now on the O atom. On the right below, the Proton from the HCN has bonded with the O^- species to form an Hydroxy /or Hydroxyl / or Hydroxide species.
- This is a **Nucleophilic Addition** reaction.



NC^- and ethanal there are now 3 C atoms in the chain counting must start from the CN

- The product that is formed is called a “Nitrile”⁵. It is an “ $\text{R}-\text{C}\equiv\text{N}$ ” species.
- Please note that the Carbonyl compound started life as an Aldehyde with **TWO** Carbon atoms – it was Ethanal. The longest Carbon chain now has **THREE** Carbon atoms in it therefore it is a “**Propanonitrile**” or “**Propanenitrile**”⁶. The C atom to which the N atom is bonded must now be regarded as the first C atom in the chain of three C atoms. The second atom in the chain has an “ $-\text{OH}$ ” species attached to it, therefore the name must state where the “ $-\text{OH}$ ” species is located (i.e. 2-hydroxy). The displayed formula can be written as $\text{CH}_3.\text{CH}(\text{OH}).\text{CN}$ and the name of this molecule is **2-hydroxy propanonitrile** or **2-hydroxypropanenitrile**.

From a Nitrile to a Carboxylic Acid

- I mentioned to you on page 1 that for organic synthesis purposes, a Nitrile is a good way into a Carboxylic Acid. (NB Please remember that in going from the Aldehyde to the Nitrile, one C atom was added to the C chain. In the example above **Ethanal** was converted to **Propanenitrile**.)
- I do not intend to go into this reaction in any detail because many intermediate species are involved, and all that I will say is that the conversion can be effected through either

a) the reversible **Acid hydrolysis** of a Nitrile into a Carboxylic Acid



or through

b) non-reversible **alkaline hydrolysis**

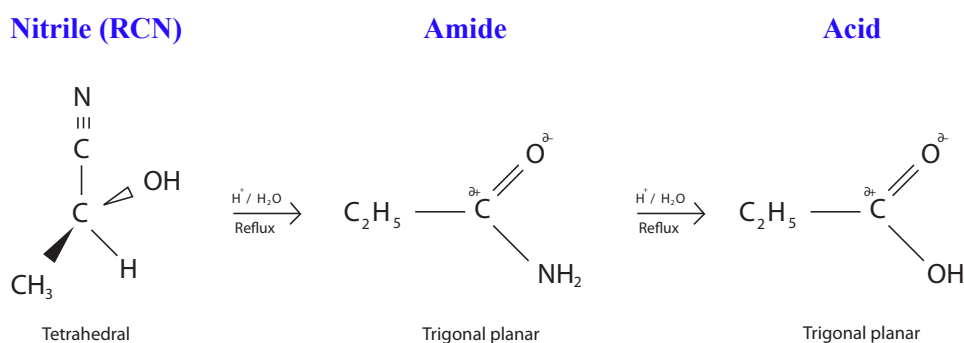


and then HCl must be added in (b) in order to convert the $\text{C}_2\text{H}_5.\text{COO}^-$ into the Carboxylic Acid $\text{C}_2\text{H}_5.\text{COOH}$. (The reaction is non-reversible because every $\text{C}_2\text{H}_5.\text{COO}^-$ ion is aquated and is thus separated from the cations.)

⁵ It is called the “cyanohydrin” of the Aldehyde.

⁶ “Propano” is the adjectival form of the noun “propane”.

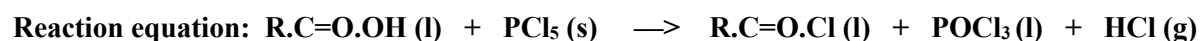
- In fact, the conversion is effected through an Amide and can be summarised thus



NB This is an extremely useful conversion in organic synthesis.

G) Reaction with PCl_5 and PCl_3 (not just toxic but **LETHAL** in high enough concentrations)

Do NOT attempt to do this yourself. Please just watch the 3-minute video at <https://www.youtube.com/watch?v=TcNFENAzUdo>. Mr Scallion (Frank Scallion) uses no more than 1cm^3 of 'glacial' ethanoic Acid⁷ and just look at the violence of the reaction. Mr Scallion spent his whole life teaching Chemistry. **He knows what he is doing, but you might hurt yourself.**



- This is a violent exothermic reaction (which is why the HCl boils off as a gas). If you put an open bottle of Ammonia near the reaction, fumes from the two substances combine to produce a white cloud of Ammonium Chloride, $\text{NH}_4\text{Cl(g)}$. (You will see that in the video.)

NB **US government hazard warning:** "Phosphorus Pentachloride is a greenish-yellow crystalline solid with an irritating odour. It is decomposed by water to form Hydrochloric and Phosphoric Acid and heat. This heat may be sufficient to ignite surrounding combustible material. It is corrosive to metals and to human tissue. Long term exposure to low concentrations or short term exposure to **high** concentrations can result in adverse health effects from inhalation."

- I would not touch either PCl_5 or PCl_3 with a bargepole!** (I do not want to go into Phosphorous Pentachloride in too much detail, but sometimes PCl_5 is a mixture of PCl_4^+ and Cl^- , and at other times it is a mixture of PCl_4^+ and PCl_6^- .⁸)
- Last year I told you that **PCl_5 can be used to test for 1° and 2° alcohols**, and that it will react **violently** with an alcohol producing choking HCl (g) therefore only a **TINY** amount of it should ever be used. Phenol will react less vigorously, and $\text{PCl}_5\text{(s)}$ will also react with water (because water dissociates a small number of OH^- ions).

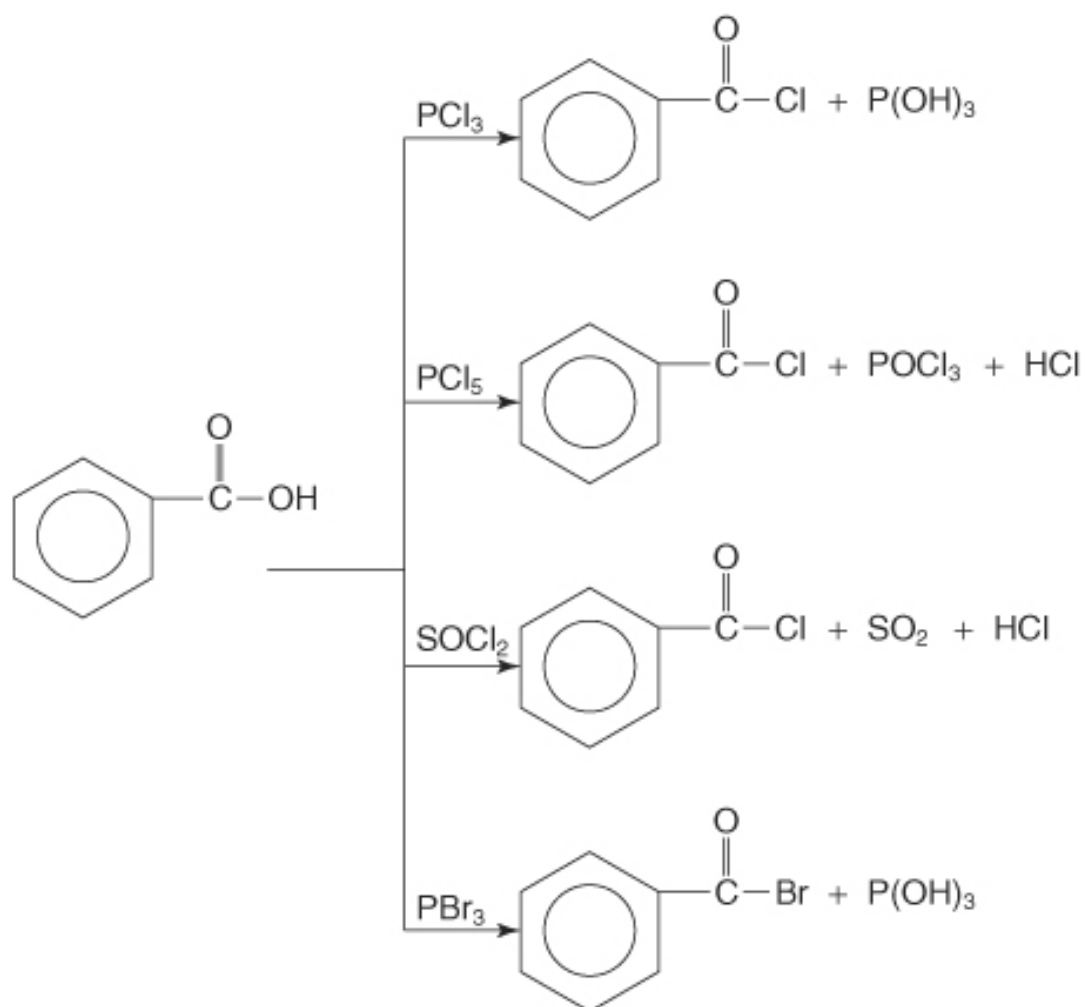
(I am not at all sure why dangerous substances are quoted as testing materials at 'A' Level. These substances are much better left for University Chemistry usage.)

- PCl_5 can also be used to convert Alcohols into
 - Acyl Chlorides (the reaction in which we are here interested)
 - Alkyl Chlorides, and into
 - Carboxylic Acids.

⁷ "Glacial" to indicate that at just 16°C it will freeze. In a cold lab, it could be solid ice.

⁸ and at 250°C in a sealed container $\text{PCl}_5 \text{ (g)} \rightleftharpoons \text{PCl}_3 \text{ (g)} + \text{Cl}_2 \text{ (g)}$.

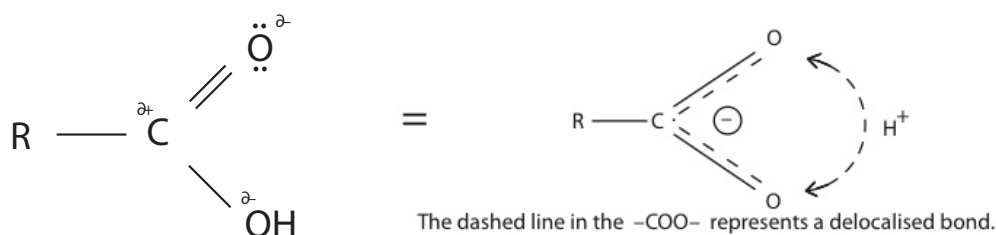
- The Chlorides and Bromides of Phosphorous can be used to convert Benzoic Acid, $C_6H_5.C=O.OH$ ($C_6H_5.COOH$) as follows



Source: CliffsNotes

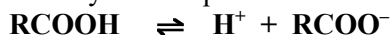
H) Carboxylic Acids are weak Acids (with pH values in the region of 3-5)

- 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 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)



where dynamic equilibrium lies **very far** to the left for a Carboxylic Acid

- but if “R” consists of an **EDG** (Electron Donating Group⁹) 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)¹⁰
 - 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.¹¹
- 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.

⁹ 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”.

¹⁰ The **weaker** an Acid, the **larger** will its pK_a and its pH be (and the more basic will it be).

¹¹ The **STRONGER** an Acid, the **SMALLER** will its pK_a and pH be.

- When a **reversible** reaction $aA + bB \rightleftharpoons cC + dD$ reaches dynamic equilibrium **at a given temperature**,¹² then there is a number/a Constant, K_c that expresses the following ratio

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{at equilibrium at a given temperature}^{13}$$

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 : $K_c \times (\text{the concentration of } H^+ \text{ ions in Water}^{14}) = K_a$.

- 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, $K_c \times (\text{concentration of } H^+ \text{ ions in Water}) = K_a = [H^+].[OH^-]$, and the concentration of H^+ cations (Protons) in pure water = the concentration of OH^- ions viz.

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

- 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” = $-\log_{10}(\text{the concentration of } H^+ \text{ ions in that substance})$, therefore from the above, the pH of pure Water = $-\log_{10}(10^{-7}) = +7$ (at 298K).
- For pure Water the
 $[H^+] = 1 \times 10^{-7} = 10^{-7}$
 $K_a = 10^{-14}$
 $pK_a = 14$, 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 $-\log_{10}([H^+])$.

¹² 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”.**

¹³ 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 $mol\ dm^{-3}$.

¹⁴ = 55.55555555 recurring = 55.5̇.

- 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".)

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	<div>↑</div>	<div>↓</div>
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 ₃ ⁻	SO ₃ 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

<http://clas.sa.ucsb.edu/staff/Resource%20Folder/Chem109ABC/Acid,%20Base%20Strength/Table%20of%20Acids%20w%20Kas%20and%20pKas.pdf>

- I know that some of you are not doing Pure Maths at 'A' level, but if you try hard you WILL see the difference between the following four things. Please therefore do try hard to 'get it'. **If you do not do so, and you go on to read Medicine, then you could end up KILLING one of your patients by accident.**
- On page 2, I pointed out (and not every textbook makes this point) that if you are going to give the pH of something, then *you have to specify the concentration of that substance* (be it 1 mol dm^{-3} / 0.1 mol dm^{-3} / 0.01 mol dm^{-3} / $0.001 \text{ mol dm}^{-3}$ / whatever mol dm^{-3}) because **the concentration WILL alter the pH value.**
- Let me now give you the same parameters for 1 mol dm^{-3} Acetic Acid as I did for pure Water

$[\text{H}^+]$	=	$0.0041686938 \approx 4.17 \times 10^{-3}$	available from any good data book
K_a	=	$0.000,0176 = 1.76 \times 10^{-5}$	available from any good data book ¹⁵
$\text{p}K_a$	=	4.75	= $-\log_{10}(1.76 \times 10^{-5})$
pH	=	2.38	= $-\log_{10}(4.17 \times 10^{-3})$.
- Just in case you have not got your brain fully into Arithmetic Mode, let me do some simple sums for you: $(0.00417) \div (1 \times 10^{-7}) = 41,700$. This is the same as $(0.00417 \times 10,000,000 = 41,700)$. Please do this on your calculator and verify that I have not made a mistake. **The concentration of H^+ ions in Acetic Acid is 41,700 times larger than the concentration of H^+ ions in pure Water.** When you are dealing with logs, **the numbers go up in powers of 10! If you do not get the Arithmetic right you can massively overdose a patient and kill her/him. Please do get your sums right.**
- As an Acid becomes STRONGER its K_a gets LARGER and its $\text{p}K_a$ gets SMALLER and its pH will get SMALLER (the smaller the pH value, the stronger will the Acid be).**
- I have now reminded you that

$[\text{H}^+]$ = the hydrogen ion concentration of something, therefore for an Acid dissolved in Water,

if $\text{HA}(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{A}^-(\text{aq})$ is at dynamic equilibrium at a given temperature,

the $K_a = \frac{[\text{H}^+].[\text{A}^-]}{[\text{HA}]}$ at equilibrium at a given temperature¹⁶

where $K_a = K_c \cdot [\text{H}_2\text{O}]$ and

$\text{pH} = -\log_{10}[\text{H}^+]$

and you can now see that you cannot create an equation linking pH and K_a without making assumptions about $[\text{H}^+]$, $[\text{A}^-]$ and $[\text{HA}]$.

- However, by looking at the table on page 12 you will see the K_a and the $\text{p}K_a$ values for many Organic Acids – and from the calculations that I have done for you, as a general rule of thumb, many Organic Acids have a $\text{p}K_a$ of about 4-5 and a pH of about 3-5.

¹⁵ But, in Inorganic Chemistry, when we get to Equilibrium constants, then I will show you how to do a good approximation of K_a from the concentration of a species.

¹⁶ The symbol " $[\text{X}]$ " 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} .

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 ₂ F.COOH	2.66
Chloroethanoic Acid	CH ₂ Cl.COOH	2.86
Bromoethanoic Acid	CH ₂ Br.COOH	2.90
Iodoethanoic Acid	CH ₂ I.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 (Propionic Acid)	C ₂ H ₅ .COOH	4.87
Butanoic Acid (Butyric Acid)	C ₃ H ₇ .COOH	4.82 (an anomalous pKa)
Pentanoic Acid (Valeric Acid)	C ₄ H ₉ .COOH	5.01
Hexanoic Acid	C ₅ H ₁₁ .COOH	4.88 (another anomaly)
Heptanoic Acid	C ₆ H ₁₃ .COOH	4.82 (another anomaly)
Phenol	C ₆ H 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 ₂ H ₅ .OH	16.0
Propanol	C ₃ H ₇ .OH	17.1

The Protons dissociated by Alcohol **attack metals** and generate H₂(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.)

- 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^{δ-} atom that holds on to the H^{δ+} 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 The first 15 Chapters of this Year’s Organic Chemistry book are on Benzene and other Arenes, therefore I have not made any reference to them in the Information Tree on page 1.

- In the next Chapter, let us look at Amides/Nitriles/Acyl Chlorides/and Acid Anhydrides.