Alkanoic Acids

Also known as **carboxylic acids**: -COOH. Carboxylic acids are the prototype organic acids. Carboxylic acids contain the **carb**onyl group and a hydr**oxyl** group, hence the name. The **carboxyl** group can be attached to an aliphatic or aromatic system.

Since alkanoic acids contain two groups, the carbonyl group, -C = O, and the hydroxyl group, -OH; thus the reactions of the carbonyl group, -C = O, are modified by the presence of the –OH, and the properties of the –OH are modified by the presence of the carbonyl group –C = O.

The alkanoic acids have been known for a long time and as a result the trivial names ascribed to them are widely used. The IUPAC names follow the usual pattern. The longest chain carrying the –C = O is considered the parent structure, and is usually named by replacing the *–ane* suffix of an alkane by *–anoic*. (The numerical position of the carboxyl group is omitted from the name of an alkanoic acid, since the carbonyl carbon atom must have the lowest number – it is the functional group – must be C_1).

Example:

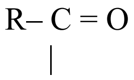
4-methylpantanoic acid

3-phenylpropanoic acid

The first two acids, methanoic acid, HCOOH, and ethanoic acid, CH_3COOH are commonly known as formic acid and acetic acid respectively (FYI-Formic acid was originally distilled from the distillate obtained from red ants, sub-family formicinae!)

The acid, C_6H_5COOH, properly named benzenecarboxylic acid, is much more widely known as benzoic acid.

Ethanedioic acid, formerly oxalic acid, is COOH– COOH. The derivatives of carboxylic acids contain the *acyl* group:



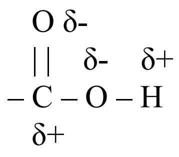
$$R-\underset{|}{C}=O$$

The Nature of the –COOH Group

Carboxylic acids are weak acids. Recall from the study of phenol that there are two principal factors that govern acidity:

1) The acidity of a compound containing a hydroxyl group X-OH is increased if X is electron-withdrawing.
2) If the anion XO^{-1} is stabilized by distributing its charge over two or more atoms.

The O-H group in a carbonyl group is polarized, due to the relative electronegativity of oxygen, such that the H is acidic and the carbon of the carbonyl carbon is electrophilic. The positive C-atom draws electrons from the –OH group increasing the positive charge on the hydrogen, and thus the likelihood of forming H^{+1} ions:



$$-\underset{\delta+}{\overset{\overset{O\ \delta-}{||}}{C}}-\overset{\delta-}{O}-\overset{\delta+}{H}$$

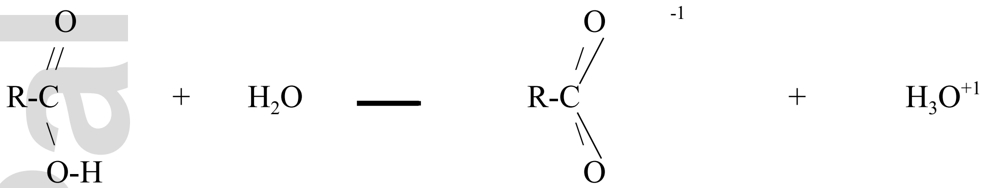
When the H^{+1} ionises off, the π-electron cloud of the carbonyl group is pulled towards the second oxygen and delocalisation of the π-electron charge occurs; i.e. the lone pair of electrons in the p-orbital also interacts with the p-orbital of the adjacent oxygen atom. Thus the charge is spread evenly across the delocalised p-orbitals. The electrons are shared equally between the two oxygen atoms and the carbon atom in the anion. Stabilization of the anion formed and the electron withdrawing effect of the O-atom helps to stabilize the $-COO^{-1}$ ion. A delocalised system, (recall: resonance energy) involves greater stability.

Electron diffraction measurements have shown the ion to be symmetrical, and the distance of each oxygen atom from the carbon atom to be intermediate between the normal lengths of the C-O and C = O bonds:

C-O 0.143 nm **C=O 0.122 nm** **C-O (in carboxylate ion) 0.127 nm**

Both C-O bonds being the same length, the anion can thus be represented as:

As with arenes, the delocalisation (two resonance forms), stabilizes the ion (i.e. lower energy), favouring the formation of the carboxylate ion in the equilibrium:



$R\text{-}C(=O)\text{-}OH + H_2O — R\text{-}C(O)(O)^{-1} + H_3O^{+1}$

acid$_1$ base$_2$ Carboxylate ion (base$_1$) (stabilized by resonance) Conjugate acid$_2$

This delocalisation helps to explain why carboxylic acids undergo hardly any of the reactions we associate with the carbonyl group.

We have seen how the acidity of the hydroxyl group is very much enhanced by the carbonyl group next to it. We will now consider how acid strength is affected by electron-attracting or electron-withdrawing substituents in the alkyl or aryl group next to the carboxyl group.

Acid Strength

The alkanoic acid donates a proton to water (which acts as a base) and is thereby converted to its conjugate base, the carboxylate ion $RCOO^{-1}$, they are therefore protonic acids and react with bases. The ionization of the acid depends on the ease of ionization of the O-H bond. The two factors which affect this ionization are:

1. The strength of the O-H bond.
2. The stability of the anion which is formed in the bond breaking process.

Alkanoic acids are much weaker than the common mineral acids. The K_a for ethanoic acid is 1.8×10^{-5} mol dm^{-3}. This means that in a 1 mol dm^{-3} solution of ethanoic acid, 3 molecules in a thousand are ionised. Substituents affect the strength of acids.

The strength of an acid in aqueous solution may be measured by its ionization constant, K_a, which is the equilibrium constant for the ionization reaction, and is consequently a quantitative measure of acid strength:

$$RCOOH \; + \; H_2O \; \text{———} \; RCOO^{-1} \; + \; H_3O^{+1}$$

$$K_a = \frac{[H_3O^+][RCOO^-]}{[RCOOH]} \qquad pK_a = -\log K_a$$

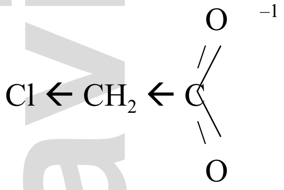
Recall: As the concentration of an acid decreases, the pH decreases, percentage dissociation increases, i.e. the acid gets stronger as it becomes more dilute; see calculations on equilibrium!

For most organic acids, K_a is small and less than 1, they are all weak acids.
A 1 mol dm^{-3} solution of ethanoic acid is less than1 % split up into ions. Ka values are ponderous to use therefore chemists prefer to use pK_a values. ($pK_a = \log 1/Ka$) The equilibrium position in this reaction depends on the relative stability of the acid and its conjugate base, so that a strong acid has a weak conjugate base and vice versa. The ionization constant of an acid may be expressed by means of a pK_a value.
Stronger acids have smaller pK_a values while weaker acids have higher pK_a values.

pK_a of Substituted Carboxylic acids

The introduction of any electron-attracting or electron-releasing group (relative to hydrogen) in the neighbourhood of the carbonyl group of a carboxylic acid would be expected to affect the strength of an acid.
The pK_a for some selected carboxylic acids are given below in Table 1.

The introduction of an electron-attracting chlorine atom in ethanoic acid, for example, will lead to greater stabilization of the substituted anion by delocalisation of the negative charge, thereby increasing the strength of the acid ($pK_a = 2.86$), whilst ethanoic acid has $pK_a = 4.76$ at 25°C:



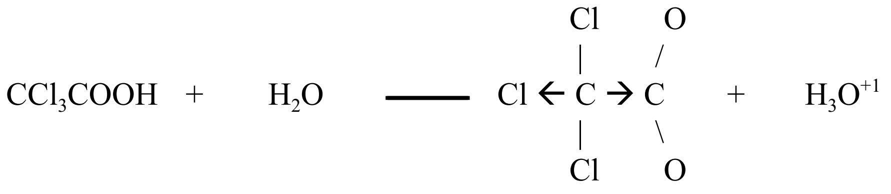
$$Cl \leftarrow CH_2 \leftarrow C\genfrac{}{}{0pt}{}{/\!/ O^{-1}}{\backslash\!\backslash O}$$

The more electronegative the substituent the greater its effect on the acid strength, hence, the effect of substituting a halogen atom in the methyl group of acetic acid, CH_3COOH is :

$$CH_2FCOOH \; > \; CH_2ClCOOH \; > \; CH_2BrCOOH \; > \; CH_2ICOOH$$

Decreasing acid strength _ --------------------->

Similarly, further substitution of chlorine atoms in the methyl group of acetic acid results in a further increase in the strength of the acid, example: trichloroacetic acid.



$$CCl_3COOH + H_2O \longrightarrow Cl \leftarrow \underset{Cl}{\overset{Cl}{C}} \rightarrow \underset{O}{\overset{O}{C}} + H_3O^{+1}$$

pKa = 0.65 (v. strong Acid)

The replacement of a hydrogen atom in the methyl group of ethanoic acid by a phenyl group (C_6H_5-) increases the acid strength, and this may be explained similarly in terms of the electron-attracting effect of the phenyl group (electron-deficient) relative to hydrogen. The following groups also have an electron-attracting effect:

- OH   - CN   >   - CO   - COOH   - NO_2

Table 1: Strengths of Carboxylic Acids at 25 ^{0}C

Acid	pKa
Methanoic (formic), HCOOH	3.75
Ethanoic (acetic), CH_3COOH	4.76
Propanoic, CH_3CH_2COOH	4.87
Trimethylacetic, $(CH_3)_3CCOOH$	5.05
Phenylacetic, $C_6H_5CH_2COOH$	4.31
Benzoic, C_6H_5COOH	4.20
Fluoroacetic (2-fluoroethanoic acid), CH_2FCOOH	2.66
Chloroacetic (2-chloroethanoic), $CH_2ClCOOH$	2.86
Bromoacetic (2-bromoethanoic), $CH_2BrCOOH$	2.90
Iodoacetic (2-iodoethanoic), CH_2ICOOH	3.17
Dichloroacetic (2,2-dichloroethanoic), $CHCl_2COOH$	1.29
Trichloroacetic (2,2,2-trichloroethanoic), CCl_3COOH	0.65

Strength of substituted ethanoic acid:

$CH_3COOH < OHCH_2COOH < CNCH_2COOH < CH_3COCH_2COOH < NO_2CH_2COOH$ $(pK_a\text{-}1.68)$

The positive inductive effect of the alkyl group, to some extent reduces the acidity of an alkanoic acid, by reducing the positive charge on the carboxyl group:

$HCOOH > CH_3COOH > CH_3CH_2COOH > CH_3CH_2CH_2COOH$

Thus, acetic acid is appreciably weaker than formic acid, but the additional methyl group in propionic acid has only a small effect on the acid strength.

The introduction of an electron-releasing alkyl group in place of hydrogen concentrates the negative charge on the carboxyl group and will therefore have the opposite effect, i.e. it reduces the polarization of the O-H bond, making the bond stronger and hence proton loss more difficult. Thus, alkyls decrease the strength of the acid by stabilization of the acid anion relative to the acid molecule.

Acid strength therefore decreases as the electron-releasing effect increases:

$$H > CH_3 > C_2H_5$$

The effectiveness of an electron-attracting or releasing group in increasing or decreasing the strength of an acid decreases rapidly with distance from the carboxyl group: (NOTE: The carbon adjacent to the carbonyl carbon is termed the α-carbon)

	β α	β α	β α
	CH_3CH_2COOH	$CH_3CHClCOOH$	CH_2ClCH_2COOH
pK_a	4.87	2.83	4.10

Substitution of chlorine in the α-position greatly increases the acid strength by inducing a δ+ charge on the carbonyl carbon. This is destabilizing and to compensate the carbonyl carbon withdraws electrons from neighbouring atoms to diminish the electron withdrawing effects of the α-carbon. This makes the O-H bond more polarized, the H more positive and more acidic. A β-chlorine atom has a much smaller effect.

In general, electron withdrawing groups increase acidity (larger K_a, smaller pK_a)

CH_2XCOOH $\qquad$ CH_2XCH_2COOH $\qquad$ $CH_2XCH_2CH_2COOH$

Decreasing order of effect of X on acid strength **----------->**

Alkanoic acids are stronger than carbonic acid, alkanoic acids will release carbon dioxide from a hydrogen carbonate.

Review questions

1. Why is acetic acid weaker than formic acid?

Acetic acid has a methyl group attached to the electropositive carbonyl. Relative to hydrogen (in HCOOH), CH3 – is an electron releasing group. This pushes electrons towards the O-H bond strengthening it, making that hydrogen less acidic (less positive = less like H^{+1})

2. Why is benzoic acid, C_6H_5COOH, a stronger acid than ethanoic acid, CH_3COOH?

Both the benzene ring and the methyl group are electron releasing, but the more important factor in this case is ion stabilization. The benzoate ion is stabilized to a greater extent than the ethanoate ion because the charge is dispersed by interaction with the delocalised ring system. Consequently, the benzoate ion accepts protons less readily and benzoic is therefore stronger.

3. **Arrange in order of increasing acid strength: phenol, benzoic acid, carbonic acid, ethanoic acid, nitrophenol**

Preparation of Alkanoic Acids

1. Oxidation of primary alcohols → aldehydes → acids

The effect of strong oxidizing agents, such as acidified MnO_4^{-1}, or $Cr_2O_7^{-2}$ on primary alcohols, aldehydes and alkyl aromatic compounds is to form acids:

What is the product when (i) 1-pentanol is reacted with $Cr_2O_7^{-2}$? (pentanoic acid)
(ii) ethanal ⟶ ethanoic acid
(iii) methylbenzene (toluene) ⟶ benzoic acid
(iv) ethylbenzene ⟶

2. Hydrolysis of nitriles

Nitriles are easily prepared from a haloalkane by treatment with the nucleophilic CN^{-1}.

(Recall: S_N1 to a 3° halogeno-alkane and/or S_N2 to a 1° halogeno-alkane).

This is a very convenient means of increasing the C-chain length in a molecule, and it also provides a useful route to alkanoic acids. The acids can be prepared by acid or alkaline hydrolysis. Alkaline hydrolysis is the easiest to bring about because it helps to eliminate the nitrogen by driving it off as ammonia, $NH_{3(g)}$.

$$\underset{\text{propanenitrile}}{CH_3CH_2\text{-}C\equiv N} + H_2O + OH^{-1} \rightarrow \underset{\text{Propanoate ion}}{CH_3CH_2COO^{-1}} + NH_{3(g)}$$

The propanoate ion, → will produce propanoic acid on acidification.

Example:

What is the product when 1-bromobutane is reacted with NaCN + conc. H_2SO_4, (–> HCN, a weak acid, .: <—> H_3O^{+1} + CN^{-1} , thus, to increase the [CN^{-1}], the reaction should be performed in acid or basic medium?)

3. From Cyanohydrins

A cyanohydrin is a molecule that has both a hydroxyl (OH) and a nitrile (CN) group in it. Cyanohydrins are usually formed by reaction of a ketone or an aldehyde with NaCN (or KCN or HCN), (Recall: Nucleophilic Addition to an alkanal or an alkanone), followed by aqueous acid to give the cyanohydrin. Hydrolysis produces an α-hydroxy acid.

Ethanal	→	2-hydroxypropane nitrile	→	2- hydroxypropanoic acid
$CH_3CHO + HCN$	→	$CH_3CH(OH)CN$	→	$CH_3CH(OH)COOH + NH_4^{+1}$
propanone	→	2-hydroxy-2-methylpropane nitrile	→	2-hydroxy-2-methylpropanoic acid
$CH_3COCH_3 + HCN$	→	$(CH_3)_2C(OH)CN$	→	$(CH_3)_2C(OH)COOH + NH_4^{+1}$

4. Hydrolysis of tri-halo compounds with aqueous alkali (NaOH)

$$CH_3CCl_3 \rightarrow CH_3\text{-}C\text{-}(OH)_3 \rightarrow CH_3COOH + H_2O$$

5. Hydrolysis of esters

Esters are hydrolysed to alcohols and carboxylic acid salts when they are boiled under reflux with aqueous alkali: $RCOOR' + NaOH \longrightarrow RCOONa + R'OH$

The carboxylic acid is obtained by acidifying the salt with a mineral acid:

$$RCOONa + HCl \longrightarrow RCOOH + NaCl$$

Chemical Reactions of Alkanoic Acids

Carboxylic acids consist of two reactive groups, the –OH, the –CO, and an alkyl or an aryl on the same carbon atom.

Reactions of the –OH group

Carboxylic acids are weak acids (<1% ionized, stronger than alcohols and phenols), they only dissociate slightly in water to form the carboxylate ion and the hydronium ion H_3O^{+1}:

$$RCOOH + H_2O \longrightarrow RCOO^{-1} + H_3O^{+1}$$

Therefore, normal acid reactions are shown:
1. They react with bases:
2. They react with active metals (Na):
3. They react with carbonate (CO_3^{-2}):
4. Acids can be halogenated with $PCl_5 \rightarrow HCl_{(g)}$
(test for $HCl_{(g)}$: gives dense white fumes with ammonia, NH_3)

Review Questions

1. Does ethanoic acid more closely resemble hydroxy or carbonyl compounds? Explain.
Ethanoic acid resembles hydroxy compounds more closely than carbonyl compounds. It reacts with Na metal and PCl_5, typical alcohol reactions, but doesn't react with 2,4-dinitrophenylhydrazine (typical of carbonyl compounds).
2. Which test indicates that ethanoic acid is stronger than phenol?
CH_3COOH releases $CO_{2(g)}$ from a carbonate , but phenol does not. Also the pH of aqueous CH_3COOH is lower than that of aqueous phenol in similar concentration.
3. Explain the fact that ethanoic acid is very soluble in water, whereas benzoic acid is only slightly soluble.
The presence of the large, non-polar benzene ring outweighs the influence of the polar carboxyl group, which participates in hydrogen-bonding with water.

Reactions of the Carbonyl Group

The carbonyl group's properties are modified by the existence of the hydroxyl group in carboxylic acids. Alkanals and alkanones have two characteristic types of reactions…
i) addition ii)addition-elimination

In both types of reactions the carbonyl compound is initially attacked by a nucleophile at the positive C-atom. However, in alkanoic acids, the carbonyl group draws charge away from the –OH group, and when it does so it reduces the charge on the C-atom. As a result the positive charge on the –CO group of acids is smaller than that on the corresponding group of alkanals and alkanones.

The positive centre is now too weak to be attacked by nucleophiles such as CN^{-1} or HSO_3^{-1} which form additional products with alkanals and alkanones. Alkanoic acids do not react with bases of the type $H_2N\text{-}X$ so no reaction with 2,4-dinitrophenylhydrazine.

Some addition-elimination reactions occur resulting in the reformation of the –C=O group. The initial stage of the reaction is the same: The nucleophile adds on to the electron deficient carbon of the C = O to give a tetrahedral intermediate. Elimination follows with the termination of the C = O bond. Ex. Esterification.

1. Estrification

The reaction of carboxylic acids with alcohols to give an ester (esterification) is an important example of a reversible reaction…

$$CH_3COOH \quad + \quad C_2H_5OH \quad \text{———} \quad CH_3COOC_2H_5 \quad + \quad H_2O \qquad K_c = 4$$

For which the equilibrium constant, K_c, at room temperature is approximately 4, therefore reaction occurs to a very small extent.

The reaction is very slow in the absence of a catalyst, but in the presence of a strong acid the carbonyl atom of the carboxylic acid is protonated to give a carbocation:

$$\overset{\overset{OH}{|}}{CH_3C} = O \quad + \quad H^+ \quad \text{————} \quad \overset{\overset{HOH}{|}}{CH_3C} = O \atop +$$

The carbocation is a more powerful electrophilic reagent than the original carboxylic acid and contains an electron-deficient carbon atom which undergoes attack by the alcohol acting as a nucleophilic reagent (note that the alcohol contains an oxygen atom with unshared pairs of electrons).
In this reaction there are two possible means of eliminating water:

The determination of which is correct is an interesting example of the use of radioisotopes. When the above reaction is carried out using alcohol which has radioactive oxygen in the molecule (isotope mass 18, ^{18}O) it is found that the water produced is not radioactive but the ester is, indicating the reaction occurs where the acyl-oxygen bond, *-OH bond of the acid must be broken* in the reaction. i.e:

The addition of a small amount of a strong acid only accelerates the rate at which the equilibrium position is reached, and displaces the equilibrium to the right, according to the Le Chatelier's Principle increasing the yield of the ester.

Note: esters are hydrolysed by water to an acid and an alcohol:

…esters react with ammonia to form amides, resulting in a peptide linkage…

$$RCOOH \xrightarrow{\qquad\quad} RCONH_2$$

2. With lithium aluminium hydride, $LiAlH_4$ or sodium borohydride, $NaBH_4$

Acids can be reduced to alcohols, a powerful reducing agent is needed to affect the reduction, $LiAlH_4$ dissolved in dry ether will affect the change.

$$RCOOH \xrightarrow{LiAlH_4 \text{ or} NaBH_4} RCH_2OH$$

Review Questions

1. Describe one simple test to distinguish between members of each of the following pairs of compounds: (a) benzaldehyde and benzoic acid (b) benzoic acid and phenol (c) ethanoic acid and benzoic acid.

2. The compounds ethanol, phenol, ethanoic acid and benzoic acid all contain the hydroxyl group, -OH.
a) i) Which of the two compounds reacts with $NaHCO_{3(s)}$?
ii) Write a balanced equation for the reaction involving one of them.
b) i) Which one of the compounds reacts with $NaOH_{(aq)}$ but not $NaHCO_{3(s)}$?
ii) Write a balanced equation for this reaction.
c) i) Which compound reacts with $Na_{(s)}$ but not with $NaHCO_{3(s)}$ or $NaOH_{(aq)}$?
ii) Write a balanced equation for this reaction.

3. in the light of your knowledge of the chemical reactions of carboxylic acids, discuss the truth of the following statement: " the reaction of the carboxyl group are typical of those of the carbonyl and hydroxyl groups that it contains". Illustrate your answer with reactions.

4. Explain why the carbonyl group in alkanoic acids is less reactive than in alkanals or in alkanones.

5. A hydrocarbon **A** does not react with chlorine in the dark. When a mixture of **A** and chlorine is irradiated with ultraviolet light two and only two monochlorinated products, **B** and **C**, are obtained. When **B** and **C** are treated separately with warm aqueous sodium hydroxide solution and then treated with potassium manganate (VII) solution, **B** gives an acid **D**, and **C** gives a ketone, **E.**
Identify **A, B, C, D** and **E**. Give your reasoning and draw their structural formulae.

6. Compounds **A, B,** and **C** are shown in order of decreasing acidity:

CH_3COOH	C_6H_5OH	CH_3CH_2OH
A	**B**	**C**

i) State what is meant by Bronsted-Lowry acid
ii) Account for the variation in acidity of compounds **A, B,** and **C.**
iii) Write an expression linking pK_a with K_a.
iv) The pK_a values of **A, B**, and **C**, but not necessarily in that order, are 10.00, 4.76 and 16.00. Assign the appropriate pK_a value to each compound.
v) Describe the expected reaction, (if any), of each of **A, B** and **C** with aqueous sodium hydroxide.
vi) Describe the expected reaction, (if any), of each of **A, B** and **C** with aqueous sodium hydrogencarbonate.
vii) State two observations you would be able to make if bromine water were added to solution **B.** Draw the structure of the organic product formed.

SOAPS

Ordinary soaps are the sodium or potassium salts of long chain carboxylic acids in fats and oils. Their general formula is $R\text{-}COO^-Na^+$, where R is a long hydrocarbon chain. It is made by the hydrolysis or sponification of fats (animal fats or fats obtained by the hydrogenation of oils) with hot NaOH or KOH:

Fat or oil + $NaOH_{(aq)}$ → Soap + 1,2,3-propantriol (glycerol or glycerine)
The most common soap, sodium stearate is prepared from animal fat (containing steric acid)..

Stearic acid + $NaOH_{(aq)}$ → Sodium stearate + 1,2,3-triol (glycerol)

(FYI: saponification is the hydrolysis of an ester to produce an alcohol and the sodium or potassium salt of an acid: $RCOOR' + NaOH \rightarrow RCOONa + R'OH$)

The soap is in the homogeneous solution which results, and is precipitated by addition of concentrated NaCl. This process is called “the salting out of soap”. The soap forms a curd and the triol remains in the lower aqueous layer.

Hard soaps consist mainly of sodium stearate. Soft soap consists of the potassium salts, they are more soluble in water. Liquid soap is a mixture of soft soap and coconut oil. Soap powders consist of powdered soap and $Na_2CO_3\mathbf{.}10H_2O$. Soaps are rather ineffective and wasteful because they react with dissolved Ca^{+2} and Mg^{+2} ions to form precipitates (called scum) such as calcium stearate, calcium octadecanoate, $(C_{17}H_{35}COO^{-1})_2\ Ca^{+2}$. Soapless detergents do not form scums in hard water because the corresponding Ca^{+2} and Mg^{+2} salts are not soluble.

Because of some disadvantages with the use of soap, scientists developed a new type of cleaning agent – *soapless detergents which instead of using animal fats, use products from crude oil.* The early synthetic detergents were non-biodegradable and polluted rivers with foam. This problem has been largely overcome by altering the hydrocarbon tails of the detergent molecules. The hydrocarbon “tails” of early detergents consisted of branched-chain polypropenes which are resistant to bacterial attack. They therefore emerged unchanged from sewage works causing damage to wildlife and often giving rise to masses of dirty foam in rivers and on seashores. Most detergents are now biodegradable; the hydrocarbon “tails” are either unbranched or have a single short branch and these are more readily broken down by bacteria.

A detergent is any substance used for washing away dirt and grease. The most common detergent is soap (BTW: the word detergent means certain synthetic products used as substitutes for soap, mostly made from alkylbenzenes, during refining of petroleum. They are sodium alkylbenzenesulphonates, the alkyl is between 10 and 18 carbon atoms. If it contains > 18, the Na salt is not soluble, if < 10 then the alkyl is not soluble enough in grease).

Detergents containing long non-polar tails but with PO_4^{-3} or SO_4^{-2} anions whose Ca^{+2} and Mg^{+2} salts are in fact water soluble and therefore do not precipitate out.

How Soap Removes Grease

The sodium salts of long hained carboxylic acids, such as sodium stearate ($C_{17}H_{35}COO^{-}Na^{+}$) behave as soaps. The ionic COO- group is at the end of an unbalanced chain of 17 carbon atoms. The long hydrocarbon chain cannot bond to water molecules and is said to be hydrophobic tail (water hating) but it mixes readily with grease and is fat-soluble. The ionic end of the molecule, COO- is in contrast hydrated by polar water molecules and so is said to be hydrophilic head (water loving). Soap can therefore mix with both water and grease.

Hydrophobic “tail” Hydrophilic “head”
\/\$COO^{-}Na^{+}$

Detergent molecules at the surface reduces the surface tension of water, because this arrangement breaks up the network of hydrogen bonding between water molecules; thus the water is able to wet materials more thoroughly.

This means that at a boundary between water and another substance (eg oil, fat, air) the ionic head of the molecule will remain in the water and the hydrocarbon tail will penetrate the other substance, grease. The grease splits up into an emulsion of tiny drops and leaves the cloth. Dirt is usually held to the cloth by grease, and therefore removing the grease also removes the dirt. With oil or fat the soap allows the formation of a suspension of small globules in water and the electrical charges (from ionic repulsion) prevent these settling so that they can be removed, hence the cleaning action of soap.

The charges on the hydrophilic groups of the detergent molecules repel each other, preventing the globules from joining together. This keeps the grease in suspension allowing it to be easily washed away.