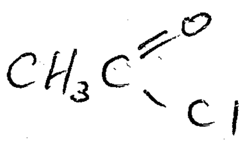
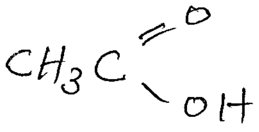
Derivative of Carboxylic acids (A2)

Acyl Chloride

e.g.



$CH_3C(=O)Cl$



$CH_3C(=O)OH$

ethano$\boxed{yl}$ chloride ethano$\boxed{ic}$ acid

Formation of Acyl Chloride

1. $CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$

ethanoic acid, phosphorus(V) chloride, ethanoyl chloride, steamy fumes

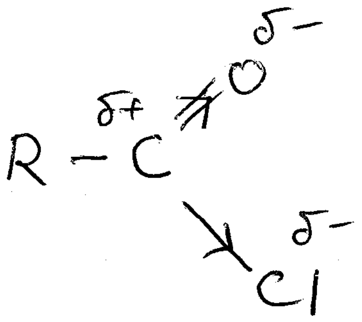
2. $CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + SO_2 + HCl$

sulfur dichloride oxide

3. $CH_3COOH + PCl_3 \xrightarrow{heat} CH_3COCl + H_3PO_3$

phosphorus (III) chloride

Acyl Chlorides – reactive compounds



both Cl atom and O atom withdrawing electrons from carbon atom. → relatively large partial positive charge on the carbon atom → highly attrative to attack by nucleophiles

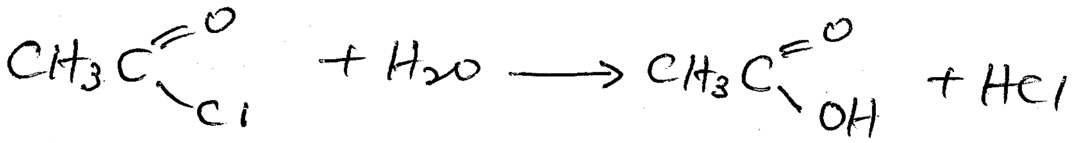
Hydrolysis of Acyl Chloride

reagent : water

condition : room temperature

products : carboxylic acids

observation : heat released (reaction is vigorous)
steamy white fumes (HCl)

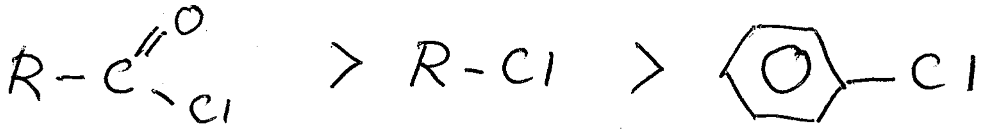


$$CH_3C(=O)Cl + H_2O \longrightarrow CH_3C(=O)OH + HCl$$

ethanoyl chloride

ethanoic acid.

Ease of hydrolysis in the order of



acyl chloride — alkyl chloride — aryl chloride

ethanoyl chloride — chloroethane — chlorobenzene

- ethanoyl chloride reacts vigorously with water.
- chloroethane reacts very slowly with water.
- chlorobenzene does not react with water
- The relative ease of hydrolysis can be followed by warming each choride with $NaOH_{(aq)}$ then by excess $HNO_{3(aq)}$ and $AgNO_{3(aq)}$.
- positive observation with white precipitate:

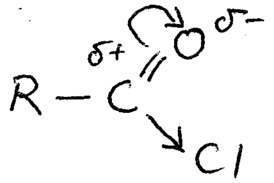
$$Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \longrightarrow AgCl_{(s)}$$

- Ethanoyl chloride gives an immediate ppt of AgCl. The reaction is more vigorous than directly with water alone.

$$CH_3COCl + OH^{-} \longrightarrow CH_3CO_2^{-} + H^{+} + Cl^{-}$$

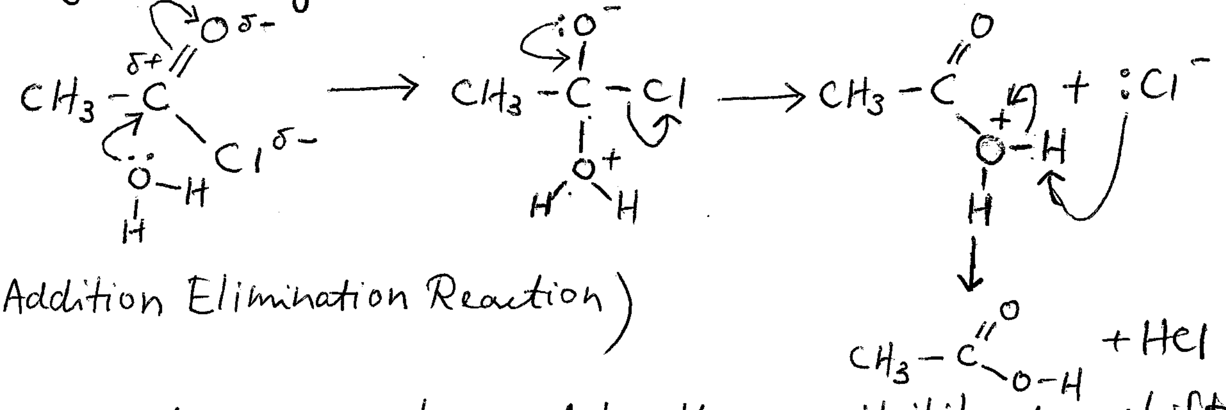
- Chloroethane gives white ppt. after some time.

- <u>Explanation</u>
- The ease of hydrolysis is depend upon the attack by nucleophiles on the δ+ carbon atoms.
- <u>Acyl chloride</u>



  - Acyl chlorides are rapidly hydrolysed by water because the chloride atom is high in electronegativity and pulls electrons away from the carbon atom of the C=O group.
  - The oxygen atom also pulls electrons from this carbon atom, so it becomes quite positive.
  - Hence a water molecule can easily form a dative bond with this carbon atom.

  e.g. <u>ethanoyl chloride</u>.

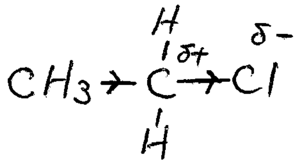


(Addition Elimination Reaction)

  - The attack is enhanced by the possibility of a shift of the π electrons in the C=O bond, which also makes it possible for the carbon atom to bond with a nucleophile before the Cl atom is released. Hence the intermediate is formed more readily.

- <u>Alkyl chloride</u>

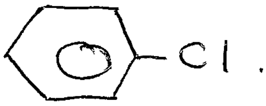
e.g. <u>Chloroethane</u>



$$CH_3 \rightarrow \overset{\overset{H}{|}\ \delta+}{\underset{\underset{H}{|}}{C}} \rightarrow \overset{\delta-}{Cl}$$

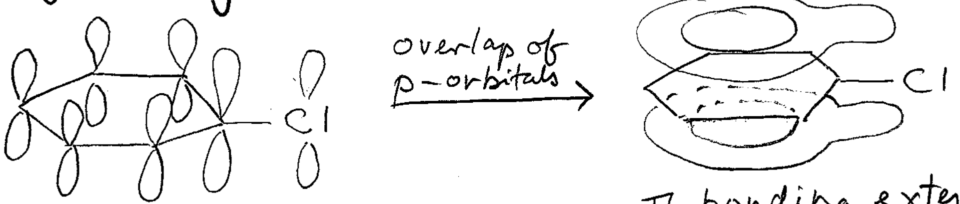
- carbon atom in a C-Cl group is attached to only one highly electronegative atom (Cl atom) and, therefore, carries a smaller partial positive charge than the carbon atom in a COCl group, which is attached to two strongly electronegative atoms.
- the methyl group has electron donating property and will reduce the partial positive charge on the carbon atom.
- Since alkyl chlorides carry a smaller positive charge on the carbon atom of the C-Cl group, they will be less susceptible to nucleophilic attack than acyl chlorides.
- Hydrolysis with water alone is very slow unless under improved conditions like added $NaOH_{(aq)}$ + heat.

- <u>Aryl chloride</u>



chlorobenze .

- benzene ring has delocalised π electrons built from overlapped of p electrons by 6 carbon atoms in the ring .
- with overlap of all p-orbitals including Cl atom, delocalised π bonding extends over Cl atom and benzene ring .



π bonding extends over Cl and benzene ring .

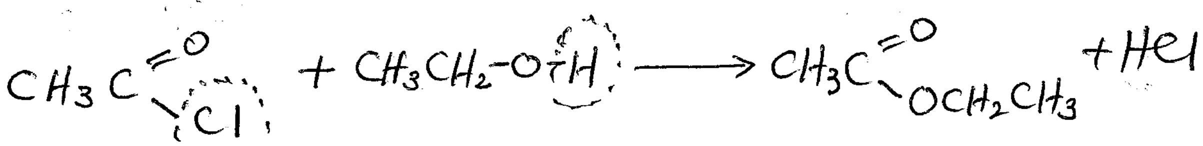
- the carbon atom attached to Cl atom is in the benzene ring . The delocalised π electron cloud is ready to compensate any partial positive charge created on the carbon atom by the Cl atom (electronegativity difference)
- the benzene ring repel any nucleophile from getting near and therefore prevent any attack by a nucleophile (eg. water molecule).

Reactions of Acyl Chloride

- due to highly partial positive charge of carbon atom at C=O group, Acyl chlorides are very reactive.
- They fumes in moist air.
- They are very reactive towards nucleophilic reagents.
- 1. Reaction with alcohols
- 2. Reaction with phenols
- 3. Reaction with ammonia
- 4. Reaction with primary amines

Reaction with Alcohols

- Reagent : alcohol
- Condition : room temperature.
- Product : ester and Hcl



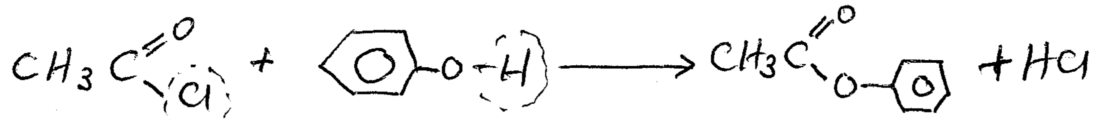
$$CH_3C\overset{=O}{\underset{\searrow Cl}{}} + CH_3CH_2-O-H \longrightarrow CH_3C\overset{=O}{\underset{\searrow OCH_2CH_3}{}} + HCl$$

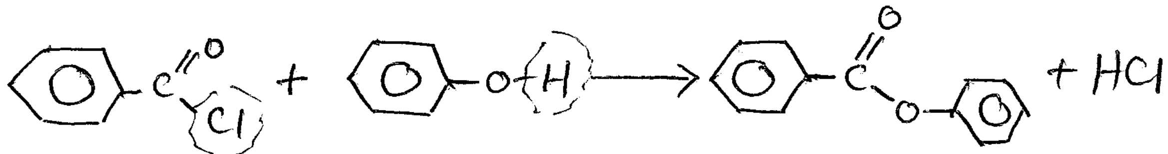
ethanoyl chloride   ethanol   ethyl ethanoate

- ethanoyl chloride react vigorously with ethanol to form an ester

Reaction with phenols

- Reagent : phenol
- Condition : warming
- products : ester and HCl .

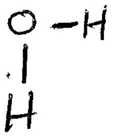


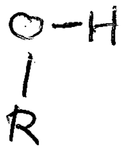


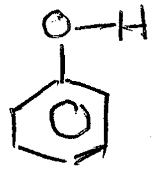
- To make phenyl esters, acyl chlorides must be used. Because there is no reaction between phenol and carboxylic acids.
- For both reactions with alcohols or phenols
  - the reaction goes to completion and do not form an equilibrium mixture.
  - they are useful in the synthesis of esters in the chemical industry.

The reaction of acyl chlorides with water, alcohols and phenols

- These reactions have similarity in chemistry.
- Comparing the structures of water, ethanol and phenol:
- each substance contains an $-OH$ group.
- In water, this is attached to a hydrogen atom.
- In an alcohol, it is attached to an alkyl group (R).
- In phenol, it is attached to a benzene ring.
  (phenol is C_6H_5OH)

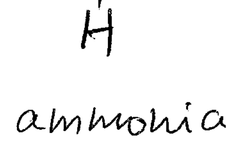






The reaction of acyl chlorides with ammonia and primary amines

- These reactions show similarity in chemistry.
- Comparing the structures of ammonia and primary amines:
- each substance contains an $-NH_2$ group.
- In ammonia, this is attached to a hydrogen atom.
- In primary amine, it is attached to an alkyl group (R) or a benzene ring

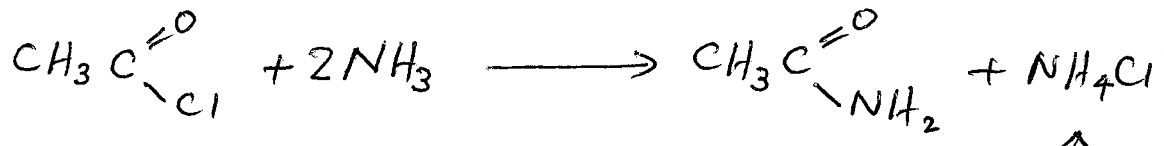


ammonia

primary amines.

Reaction with Ammonia

- Reagent : Ammonia (concentrated)
- Condition : Room temperature
- Product : Amides



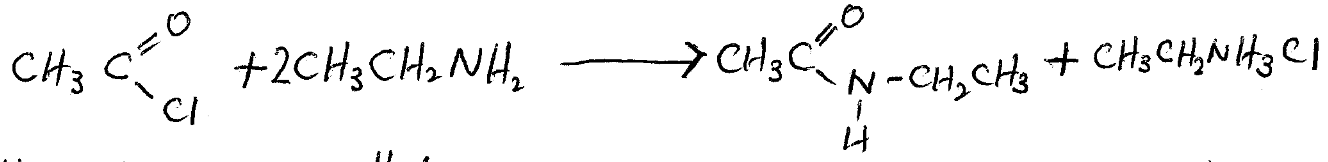
$$CH_3C(=O)Cl + 2NH_3 \longrightarrow CH_3C(=O)NH_2 + NH_4Cl$$

ethanoyl chloride   ethanamide

- violent reaction producing lot of white smoke.

Reaction with Primary Amines

- Reagent : primary amine (concentrated)
- condition : room temperature
- Product : N- substituted amides.



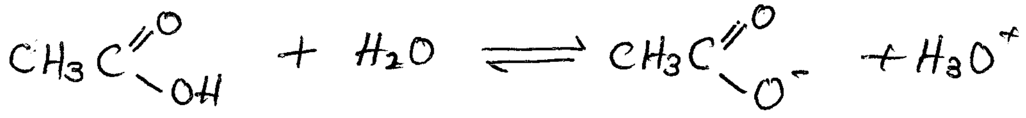
$$CH_3C(=O)Cl + 2CH_3CH_2NH_2 \longrightarrow CH_3C(=O)NH-CH_2CH_3 + CH_3CH_2NH_3Cl$$

ethanoyl chloride   ethylamine   N-ethyl ethanamide   ethylammonium chloride

- The reaction is vigorous.

The acidity of carboxylic acids

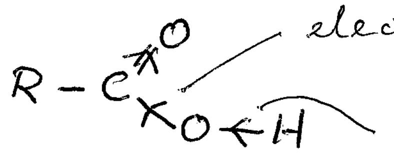
- carboxylic acids are weak acids.
- but carboxylic acid is a stronger acid compared to alcohol and phenol.
- when ethanoic acid dissolves in water,



$$CH_3C(=O)OH + H_2O \rightleftharpoons CH_3C(=O)O^- + H_3O^+$$

ethanoic acid — ethanoate ion.

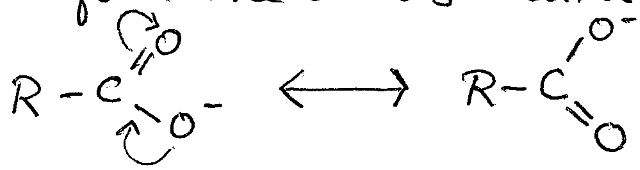
- K_a (25°C) = 1.7×10^{-5} mol dm^{-3}, the position of this equilibrium lies over to the left-hand side. Small K_a value ⟶ weak acid.
- The O–H bond in the carboxylic acid is weakened by the C=O group:



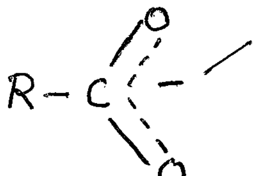
electrons in the C–O bond are drawn towards the C=O bond.

electrons are drawn away from the O–H bond.

- The carboxylate ion is stabilised by delocalisation of electrons around the –COO⁻ group. This delocalisation spread out the negative charge on the carboxylate ion, making it less likely to bond with an $H^+_{(aq)}$ ion to reform the undissociated acid molecule.



i.e.



negative charge is spread over the whole –COO⁻ group (the bond lengths of both carbon–oxygen bonds are equal)

Relative Strength of Carboxylic Acids

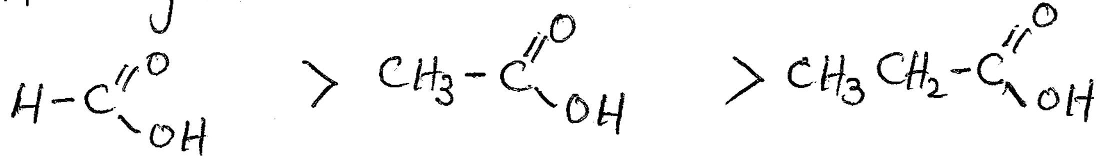
- The strength of a carboxylic acid is affected by the nature of the substituent group.

- Substituent group can be either:
  1. electron-donating group – decreases acid strength
  2. electron-withdrawing group – increases acid strength

Electron-donating group decreases the acid strength of carboxylic acid.

- electron-danating group intensifies the negative charge on the O atom, making the carboxylate ion less stable. Carboxylate ion prefers to associate back with H^+ ion to form undissociated carboxylic acid molecule.

- Acidity:



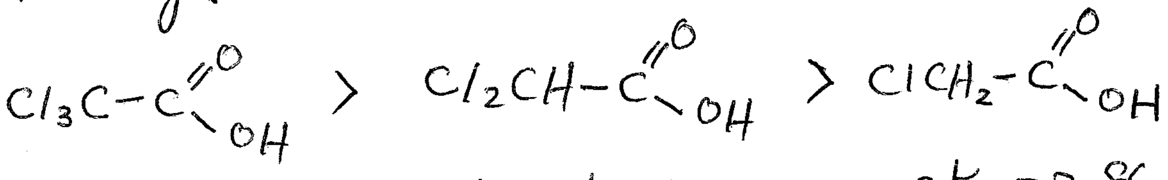
$HCOOH > CH_3COOH > CH_3CH_2COOH$

pKa = 3.77　　pKa = 4.76　　pKa = 4.88

- The greater the electron-donating effect, the weaker is the acid.

Electron-withdrawing group increases the acid strength of carboxylic acids

- electron-withdrawing group helps to reduce the negative charge gathered on O atom, thus stabilises the carboxylate ion and weakening the O-H bond.
- these improve the readiness of carboxylic acid to dissociate and form carboxylate ion and H^+ ion.
- Acidity:



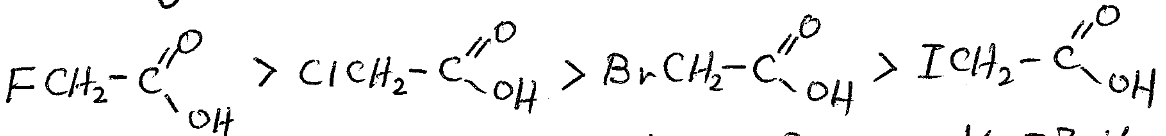
$Cl_3C-C(=O)OH > Cl_2CH-C(=O)OH > ClCH_2-C(=O)OH$

$pK_a = 0.65$ $pK_a = 1.29$ $pK_a = 2.86$

- The greater the electron-withdrawing effect (with higher number of electron withdrawing group), the stronger is the acid.

The acidity of halogen-substituted ethanoic acid

- The acidity increases when the substituted halogen is more electronegative.
- Electronegativity : F > Cl > Br > I
- Acidity :

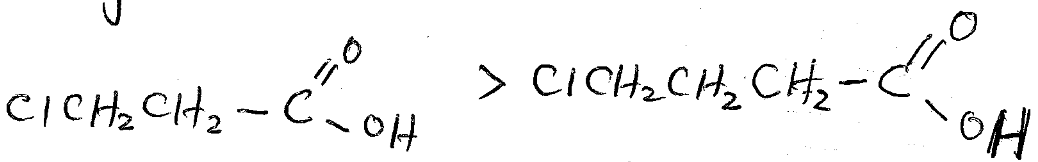


$FCH_2-C(=O)OH > ClCH_2-C(=O)OH > BrCH_2-C(=O)OH > ICH_2-C(=O)OH$

pKa = 2.66 pKa = 2.86 pKa = 2.89 pKa = 3.16

The distance of the substituent group from carboxyl group

- the distance of the substituent group from the carboxyl group increases, the acidity decreases.
- Acidity :



$ClCH_2CH_2-C(=O)OH > ClCH_2CH_2CH_2-C(=O)OH$

pKa = 4.05 pKa = 4.53

- The same understanding applies for the aromatic acids. The electron-withdrawing groups increases the acidity of the aromatic acids.