

## Carboxylic Acids<sup>1</sup> and Derivatives

GF of monocarboxylic acids:  $RCO_2H$ , if aliphatic-  $C_nH_{2n}O_2$

Physical Properties:

- Liquid/ solid at rtp
- Boiling point increases as no of C atoms increases  
→ strength of id-id i between R groups increases
- Have higher boiling point compared to alcohol of similar Mr  
→ more sites for formation of hb → more extensive hb  
→ stronger hb → O-H bond in -COOH more polar due to the presence of electron withdrawing carbonyl group<sup>2</sup>

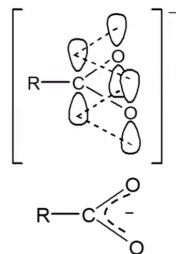
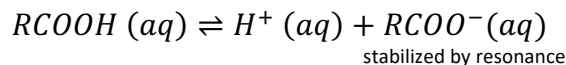
- Solubility in water decreases, solubility in non-polar solvents increases as length of non-polar hydrocarbon chain increases

Benzoic acid dissolves readily in hot water but is only slightly soluble in cold water. White ppt of benzoic acid appears when the hot solution is cooled

- Can form dimers through hb formation between 2 molecules

Acid Strength:

Depends on **stability of anion** formed



<sup>1</sup> Example: CA: Propanoic acid, Salt: propanoate

<sup>2</sup> Due to greater electron deficiency of H atom of -OH group, resulting in stronger attractive force between electron deficient H atom and lone pair of e on another molecule

Explanation:

1. Order of acid strength
2. Electron donating/ withdrawing effect
3. Effect (intensify/ disperse) negative charge on  $-COO^-$  group
4. Stability of anion

E.g. Electronegativity and electron withdrawing effect increases from I to Br to Cl to F. F being the most electronegative and the most electron withdrawing, it disperses the negative charge on  $-COO^-$  group on most effectively among the 4 halogen atoms.  $CH_2FCOO^-$  is the most stable anion followed by  $CH_2ClCOO^-$ ,  $CH_2BrCOO^-$ ,  $CH_2ICOO^-$ . Hence,  $H_2FCOOH$  is the most acidic followed by  $CH_2ClCOOH$ ,  $CH_2BrCOOH$ ,  $CH_2ICOOH$ .

Negative charge on  $-COO^-$  group is dispersed **most effectively**, with more electronegative halogen and proximity of electron withdrawing group with the  $-COO^-$  group.

Note: Benzoic acid is stronger than some aliphatic acids due to delocalisation<sup>3</sup> of negative charges of benzoate anion into the benzene ring → benzoate anion more stable than some carboxylate anion

Acid strength: ethanol < water < phenol < carboxylic acids < mineral acids

<sup>3</sup> condition: overlap of orbitals. ≠ dispersion, where the condition is attractive force of an electron withdrawing atom

Preparation:

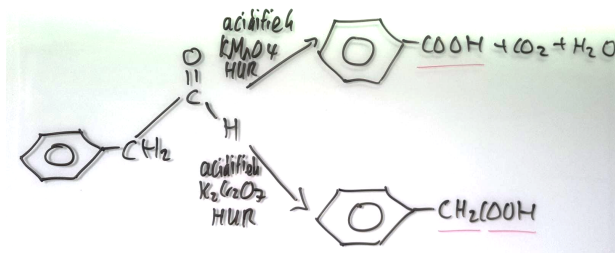
1. **Oxidation** of primary alcohols and aldehydes (Hydroxyl Compounds)

R/C: Acidified  $KMnO_4$  or acidified  $K_2Cr_2O_7$ , HUR

2. **Oxidation** of alkyl benzenes (Arenes)

R/C: Acidified  $KMnO_4$ , HUR

For 1 and 2, when reactant has a BR, using acidified  $KMnO_4$  or acidified  $K_2Cr_2O_7$  will affect the type of product formed.



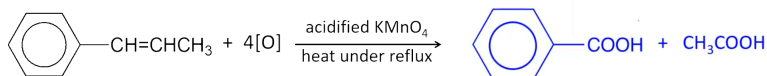
It is easier to oxidize primary alcohol than an alkyl group on BR side chain.

3. **Oxidation** of alkenes with structure  $RCH=CHR'$  (Alkenes)

Involve cleavage of  $C=C$

R/C: Acidified  $KMnO_4$ , HUR

Example:



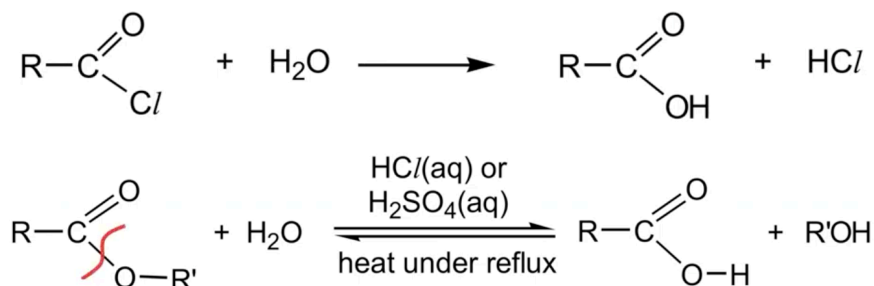
4. **Hydrolysis** of nitriles (Halogen Derivatives)

R/C:

① Acidic Hydrolysis: Dilute  $HCl$  (aq)/  $H_2SO_4$  (aq), HUR

② Alkaline Hydrolysis + Acidification:  $NaOH$  (aq), HUR, followed by dilute  $HCl$  (aq)/  $H_2SO_4$  (aq)

5. **Hydrolysis** of acyl chlorides and esters



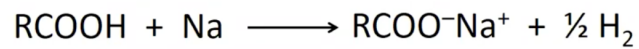
Reactions:

Electron deficient carboxyl carbon is susceptible to attack by nophile, but less susceptible to attack by nophile as compared to carbonyl carbons of ketones and aldehydes

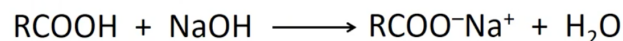
Lone pair in p orbital of O atom of -OH group can be **delocalised** into  $\pi$  bond of  $-C=O$  group  $\rightarrow$  **drift of electron density** from O atom of -OH group towards the electron deficient carbon  $\rightarrow$  **reduce the partial positive charge** on carboxyl carbon

Reactions involving cleavage of O-H bond:

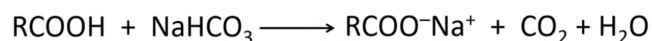
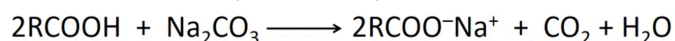
1. Reaction with reactive metal



2. Reaction with bases



3. Reaction with  $\text{CO}_3^{2-}$  or  $\text{HCO}_3^-$



Allows for carboxylic acids to be distinguished from phenols and alcohols.

Observation:  $\text{CO}_2(\text{g})$  evolves forms white ppt with limewater.

As mineral acids are stronger than carboxylic acid, addition of mineral acid converts the salt of carboxylic acid back to the original acid.

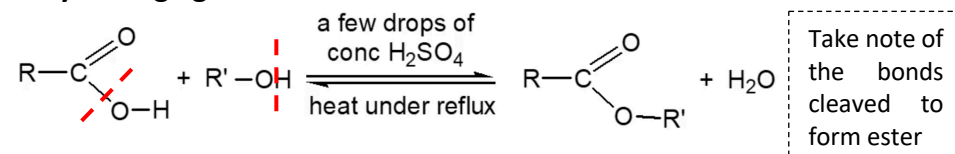
N.B. Carboxylic only exhibit acidic property in aq medium. Reactions 2 and 3 occurs only in aqueous medium. But reaction 1 may still happen in non-aqueous mediums.

Reactions involving cleavage of C-O bond:

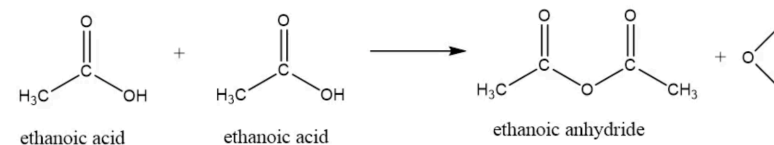
4. **Condensation** reaction to form ester (Hydroxyl Compounds)

R/C: Alcohol, a few drops of con  $\text{H}_2\text{SO}_4$ , HUR

Purpose of con  $\text{H}_2\text{SO}_4$ : **Catalyst** to protonate carboxylic acid, **dehydrating agent** to remove water and favour fwd rxn

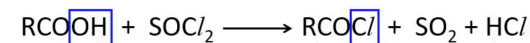
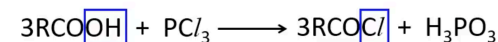
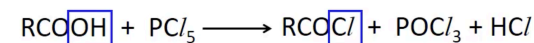


5. **Condensation** reaction to form acid anhydride from 2 carboxylic acids



6. **Nucleophilic substitution** to form acyl chlorides

R/C:  $\text{PCl}_5$  or  $\text{PCl}_3$  or  $\text{SOCl}_2$ , room temperature

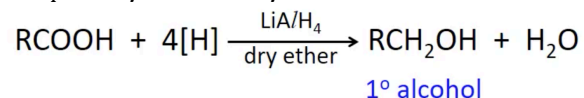


HCOOH does not form acyl chloride. This is because  $\text{HCOCl}$  is highly unstable and decomposes to give  $\text{CO}$  and  $\text{HCl}$ .

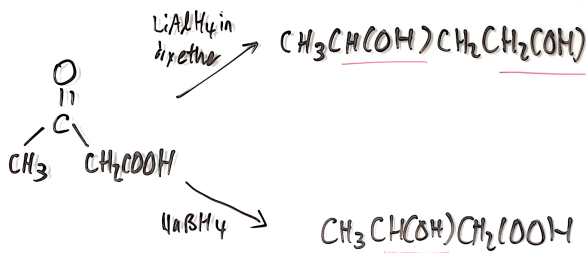
Others:

7. **Reduction** of carboxylic acid

R/C:  $\text{LiAlH}_4$  in dry ether only

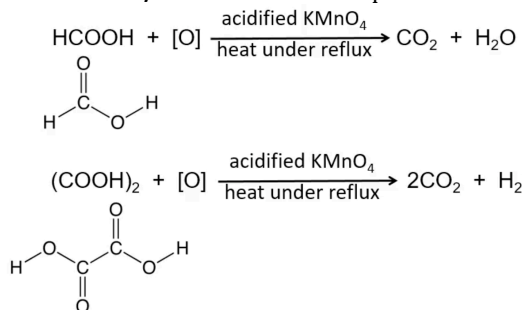


If  $\text{NaBH}_4$  is used, it will allow for selective reduction.



8. Special Cases: Methanoic Acid and Ethanedioic Acid

a. **Oxidation** by acidified  $\text{KMnO}_4$



- b. Methanoic Acid is able to give false +ve test with Fehling's reagent and Tollen's reagent, as it has an aldehyde group and is easily oxidised.

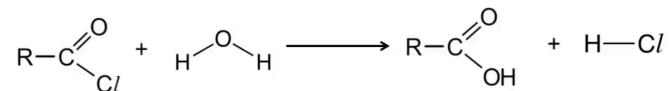
**Carboxylic Derivatives:**

Derivatives	Nomenclature	Physical properties
Acyl chlorides	ethanoic acid to ethanoyl chloride	Boiling point lower than carboxylic and alcohols of comparable Mr.
Esters	ethyl (alkyl group attached to O) ethanoate (carboxylic acid portion)	→ pd-pd i between molecules Acyl chlorides soluble in water. Esters slightly soluble (up to 5C). Esters are isomeric with carboxylic acids.
Amides	3-bromobenzoic acid to 3-bromobenzamide	Boiling point higher than carboxylic and alcohols of comparable Mr. Fairly soluble in water. → hb between molecules All are white crystalline solid at rtp except methanamide (I).
Acid anhydride	Ethanoic propanoic (name of acid w/o 'acid') anhydride  If 2 acids are the same, e.g. ethanoic anhydride.	

Reactions:

Acyl chlorides

1. Hydrolysis/ Nucleophilic Substitution (Vigorous rxn)



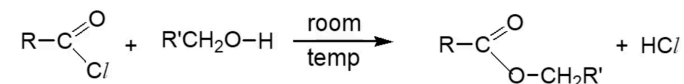
Observation: Moist blue litmus paper turns red. When  $\text{AgNO}_3(\text{aq})$  is added to resulting solution, white ppt of  $\text{AgCl}$  is formed immediately.

Distinguishing test for acyl chlorides

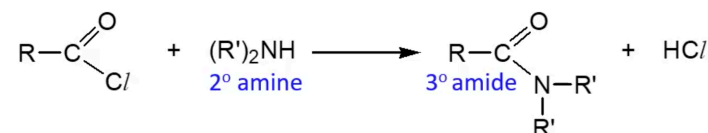
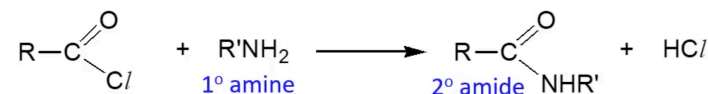
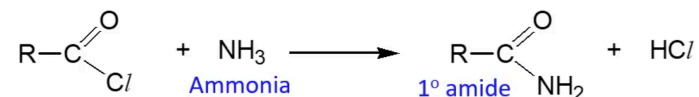
N.B. Benzoyl chloride is less reactive than alkyl acyl chlorides.  
Reason: Delocalisation of electron density between p orbital of Cl atom,  $\pi$  bond in  $\text{C}=\text{O}$  group and  $\pi$  electron cloud of BR  $\rightarrow$  reduce partial positive charge on carbonyl carbon

Ease of hydrolysis	$\text{RCOCl} >$	$\text{RCH}_2\text{Cl} >$	$\text{C}_6\text{H}_5\text{Cl}$
R/C	$\text{H}_2\text{O}$ , room temp	$\text{NaOH (aq)}$ , heat	No rxn
Reason	Carbonyl carbon in $-\text{COCl}$ is <u>highly electron deficient</u> , as it is bonded to 2 electronegative atoms, hence <u>easily attacked by nucleophiles</u>	Carbon atom of $\text{C}-\text{Cl}$ <u>less electron deficient</u> than in $\text{RCOCl}$	Stronger $\text{C}-\text{Cl}$ bond with <u>partial double bond character</u>

2. Condensation reaction to form ester (Hydroxyl Compounds)



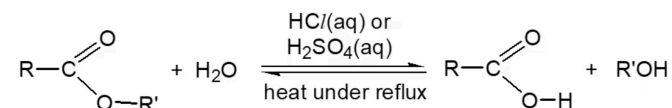
3. Condensation reaction to form amide



Ester (reversing formation of ester)

1. Acidic Hydrolysis

R/C: Dilute  $\text{HCl}(\text{aq})$  or  $\text{H}_2\text{SO}_4(\text{aq})$ , HUR



Hydrolysis is slow if not catalysed

$\text{OH}^-$  is a stronger nucleophile  
Irreversible due to resonance stabilized carboxylate ion

2. Alkaline Hydrolysis

R/C:  $\text{NaOH (aq)}$ , HUR

