CW

Unit-14

Carboxylic Acid and it's derivatives

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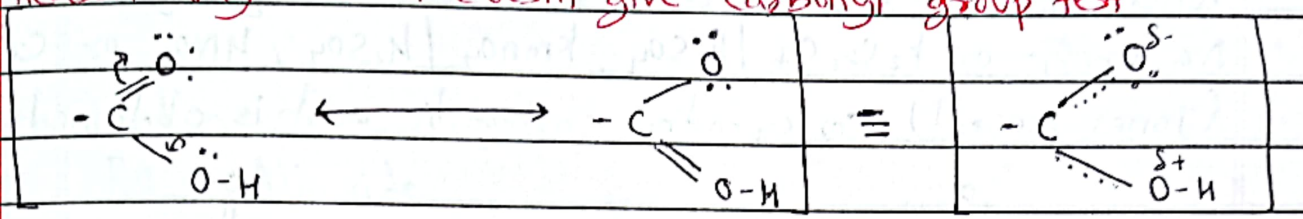
Resonance structure of $-\overset{O}{\overset{\|}{C}}-OH$ group

OR

Reason Why $-\overset{O}{\overset{\|}{C}}-OH$ doesn't give carbonyl group test



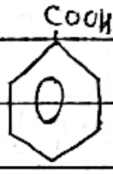
(I) (II) Resonating Hybrid

Resonating structure

Classification on the basis of number of -COOH present

$H-\overset{O}{\overset{\|}{C}}-OH$
formic Acid
(Methanoic Acid)

$CH_3\overset{O}{\overset{\|}{C}}-OH$
Acetic Acid
(Ethanoic Acid)



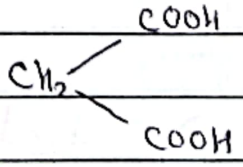
Benzoic Acid

Cinnamic Acid

Dicarboxylic Acid

COOH
COOH
Oxalic Acid
(Ethan-1,2 dioicacid)

CH_2COOH
CH_2COOH
(succinic Acid)



Tricarboxylic Acid

CH_2-COOH
$HO-C-COOH$
CH_2-COOH
(citric Acid)

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General Method of Preparation

1. From oxidation of Aldehyde

When aldehydes are treated with oxidizing agents such as $Na_2Cr_2O_7$ or $K_2Cr_2O_7/H_2SO_4$, $KMnO_4/H_2SO_4$, HNO_3 or CrO_3/H^+ (Jones reagent) corresponding carboxylic acid is obtained.

$$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}H \xrightarrow{CrO_3/H^+} CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}-OH$$

(Butanal) (Butanoic Acid)

→ Tollen's reagent $(Ag(NH_3)_2).OH$ and fehling reagent (CuO) even can oxidize aldehyde to carboxylic acid

2. Hydrolysis of cyanide / Nitrile

On complete acidic hydrolysis of cyanide, carboxylic acid is obtained

$$R-C\equiv N \xrightarrow{2H_2O/HCl} R-\overset{O}{\overset{\|}{C}}-OH + NH_4Cl$$

Example:

$$CH_3CH_2-C\equiv N + H_2O \xrightarrow{HCl} CH_3CH_2-\overset{O}{\overset{\|}{C}}-NH_2$$

(Propanamide)

$$CH_3CH_2-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{H_2O/HCl} CH_3CH_2-\overset{O}{\overset{\|}{C}}-OH + NH_4Cl$$

(Propanoic acid)

3. Dehydration of dicarboxylic Acid

→ When dicarboxylic acid is heated, one CO_2 gas is evolved to give monocarboxylic acid.

→ Also called decarboxylation reaction.

$$CH_2(COOH)-COOH \xrightarrow[\Delta]{160C} CH_3-COOH + CO_2\uparrow$$

Acetic acid

(Ethanoic Acid)

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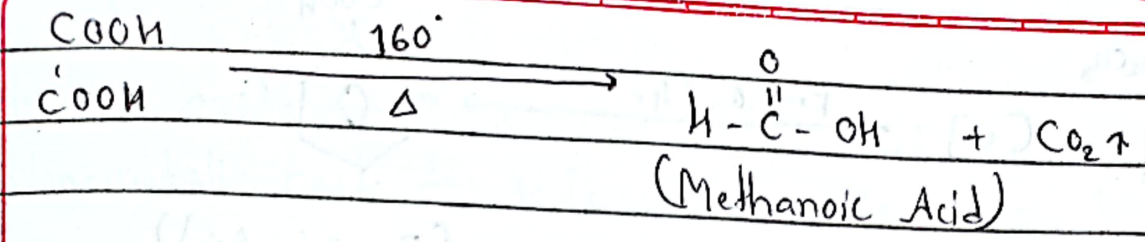
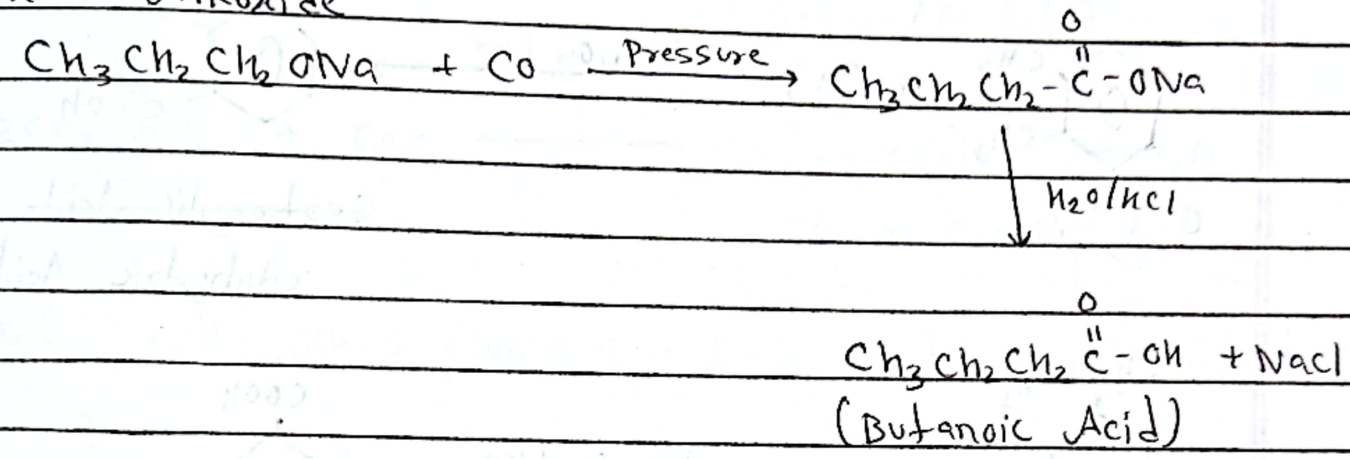


4. Action of Sodium Alkoxide with carbon monoxide

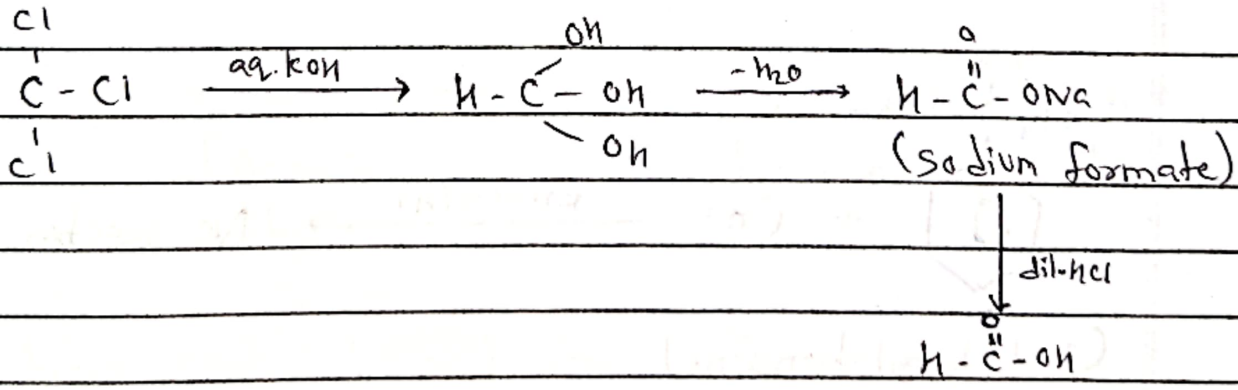
RO = Alkoxide



5. By hydrolysis of haloalkanes (chloroform)

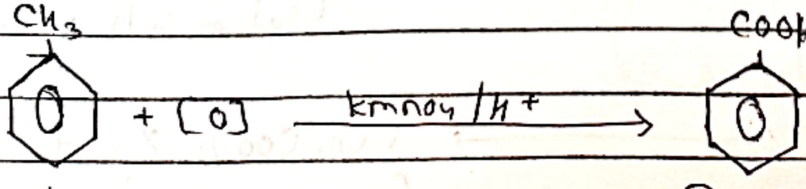
→ When trihaloalkane (chloroform) is treated with aq. NaOH or KOH, alkantriol is formed which release H_2O to form carboxylic Acid.

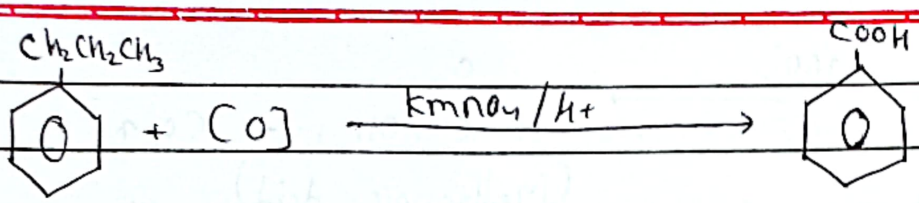
Example:



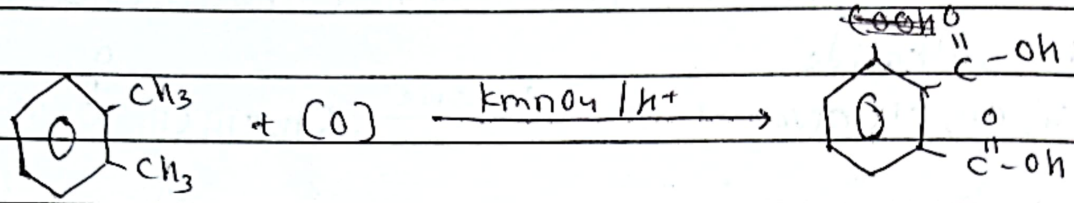
Preparation of Aromatic carboxylic Acid (Benzoic Acid)

↳ Oxidation of alkyl benzene by $KMnO_4/H^+$, $K_2Cr_2O_7/H^+$ etc. converts the alkyl group to -COOH irrespective to ther chain.

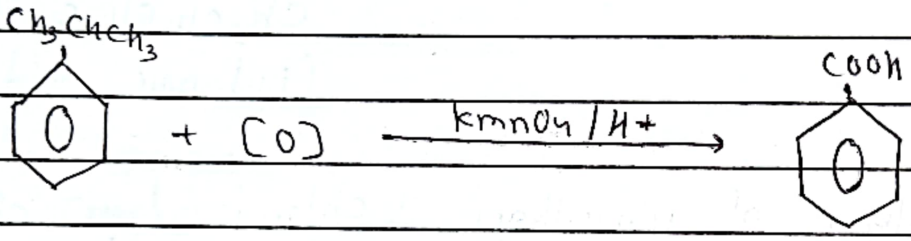




(Propyl benzene) (Benzoic Acid)

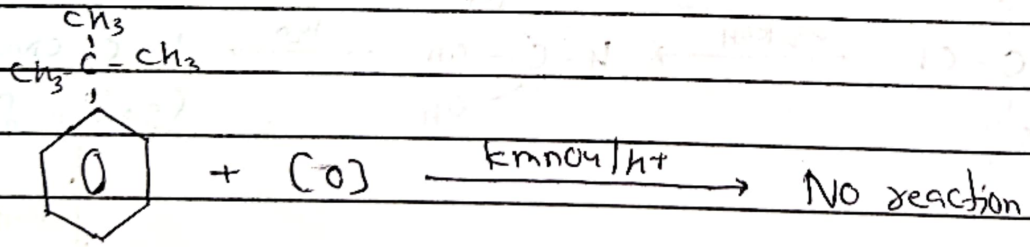


O-xylene ~~Carboxylic Acid~~ Anhydric Acid



ISO-propyl benzene Carboxylic acid

Note: Text-butyl benzene doesn't show oxidation due to the absence of 3°H:



(Text-butyl benzene)

Chemical Properties of Mono carboxylic Acid.

1. Action with Metals (Na, k, Ca, Zn, Mg etc.)

$2CH_3COOH + 2Na \longrightarrow 2CH_3-C(=O)-ONa^+ + H_2\uparrow$

(Sodium salt of carboxylic Acid)

$2CH_3COOH + Zn \longrightarrow (CH_3COO)_2.Zn + H_2\uparrow$

(Zinc Acetate)

2. Reaction with Metallic oxide

Metallic oxide ⟶ Basic oxide ⟶ Na_2O, MgO, CaO etc.

Non-metallic oxide ⟶ Acidic oxide ⟶ CO_2, NO_2 etc.

$2CH_3COOH + Na_2O \longrightarrow 2CH_3COONa + H_2O$

Acetic Acid (Sodium Acetate)

$2CH_3COOH + CaO \longrightarrow (CH_3COO)_2Ca + H_2O$

(calcium acetate)

3. Action with Alkali (NaOH, KOH, NH_4OH etc)

$R-\overset{O}{\overset{\|}{C}}-OH + NaOH \longrightarrow R-\overset{O}{\overset{\|}{C}}-ONa + H_2O$

(Acid) (Alkali) (Sodium salt of carboxylic Acid)

$CH_3-\overset{O}{\overset{\|}{C}}-OH + NaOH \longrightarrow CH_3\overset{O}{\overset{\|}{C}}-ONa + H_2O$

(Sodium Acetate)

$CH_3-\overset{O}{\overset{\|}{C}}-OH + NH_4OH \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-ONH_4 + H_2O$

(Ammonium -hydroxide) (Ammonium Acetate)

VVI But, When carboxylic acid reacts with ammonia

i. Ammonium acetate is formed which on heating decompose to give amide.

$CH_3-\overset{O}{\overset{\|}{C}}-OH + NH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-ONH_4 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + H_2O$

(Ethanoic Acid) {Ammonium Acetate} (Ethanamide)

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4. Reaction with Carbonate and Bicarbonate

→ Reaction to distinguish carboxylic acid from phenol

→ Carboxylic acid can decompose carbonate or bicarbonate but phenol does not.

→ During decomposition of CO_2 effervescene is seen.

$$2CH_3-\overset{O}{\overset{\|}{C}}-OH + Na_2CO_3 \longrightarrow 2CH_3-\overset{O}{\overset{\|}{C}}-ONa + CO_2\uparrow + H_2O$$

$$CH_3\overset{O}{\overset{\|}{C}}-OH + NaHCO_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-ONa + CO_2\uparrow + H_2O$$

5. Reaction with PCl_5 ~~or~~ $\overset{\Delta}{}$ PCl_3

$$3CH_3COOH + PCl_3 \xrightarrow{\text{Pyridine}} 3CH_3-\overset{O}{\overset{\|}{C}}-Cl + H_3PO_3$$

$$CH_3CH_2\overset{O}{\overset{\|}{C}}-OH + PCl_5 \xrightarrow{\text{Pyridine}} CH_3CH_2\overset{O}{\overset{\|}{C}}-Cl + POCl_3 + HCl$$

$$R-\overset{O}{\overset{\|}{C}}-OH + SOCl_2 \xrightarrow{\text{Pyridine}} R-\overset{O}{\overset{\|}{C}}-Cl + HCl + SO_2$$

Note:

Best to use $SOCl_2$ in pyridine as pure acid halide is obtained.

6. Dehydration of carboxylic acid

→ Intermolecular dehydration of carboxylic acid occurs resulting acid anhydride.

→ Dehydrating agent such as P_2O_5, conc. H_2SO_4 can be used.

Note:

Dehydration of formic acid gives CO and H_2O but not anhydride.

$$R-\overset{O}{\overset{\|}{C}}-OH$$
$$\overset{O}{\overset{\|}{R-C}}-OH \quad + P_2O_5 \text{ or conc. } H_2SO_4 \longrightarrow R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$$

Acid Anhydride

But,

$$H-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\Delta]{P_2O_5} CO + H_2O$$

7. Reaction due to $-\overset{O}{\overset{\|}{C}}$ group of carboxylic acid

→ Carboxylic acid doesn't shows characteristic reaction of aldehyde and ketone but $-\overset{O}{\overset{\|}{C}}$ of carboxylic acid can be reduced to CH_2 giving alcohol as final product.

→ Reducing agent used are (i) $LiAlH_4$
(ii) B_2H_6
(iii) H_2 in presence of $CuCr_2O_4$

$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[H_2/CuCr_2O_4]{B_2H_6} R-CH_2-OH \quad (\text{Alcohol})$$

Example:

$$CH_3CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[B_2H_6 \text{ or } CuCr_2O_4]{LiAlH_4} CH_3CH_2CH_2OH \quad (\text{Propanol})$$

8. Reaction due to (R-) alkyl group of carboxylic Acid

VI → α-halogenation of aliphatic carboxylic acid called Hell-Volhard-Zelinsky reaction. (HVZ reaction)

→ When carboxylic acid is treated with halogen (Cl and Br) but not (fl, I) in the presence of red phosphorus are having α-hydrogen, reaction occurs till all replacement of α-hydrogen by halogen take place.

→ Methanoic acid ~~due to~~ doesn't contain α-hydrogen and doesn't give HVZ reaction.

→ HVZ reaction is used to increase the acidity of carboxylic acid. Example:

$CCl_3-\overset{O}{\overset{\|}{C}}-OH$ is more acidic than $CH_3-\overset{O}{\overset{\|}{C}}-OH$

$CH_3-\overset{O}{\overset{\|}{C}}-OH + Cl_2 \xrightarrow[\Delta]{\text{red phosphorous}} CH_2Cl-\overset{O}{\overset{\|}{C}}-OH + Cl_2 \xrightarrow{\text{red phosphorous}} CHCl_2-\overset{O}{\overset{\|}{C}}-OH$

$CHCl_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\text{red phosphorous}} CCl_3-\overset{O}{\overset{\|}{C}}-OH$

(2,2,2-trichloro ethanoic acid)

Reaction of Aromatic carboxylic acid (Benzoic Acid)

Reaction due to carboxyl group (COOH)

i. Acidic Nature

$C_6H_5COOH > HCOOH > CH_3COOH$

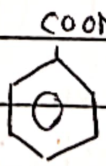
→ Benzene has resonance

→ Benzene itself is electron withdrawing group

→ Formic acid has no electron releasing group

→ Ethanoic acid contain electron releasing group (CH_3)

Reaction shown by Benzoic Acid due to Acidic Nature

- NaOH / KOH, Neutralization →  + H_2O
- C_2H_5OH / conc. H_2SO_4, esterification →  (Ethyl Benzoate)
- $LiAlH_4$ / ether, reduction →  (Benzyl alcohol)
- NH_3 → ~~C_6H_6~~
- CaO / NaOH, Δ → C_6H_6

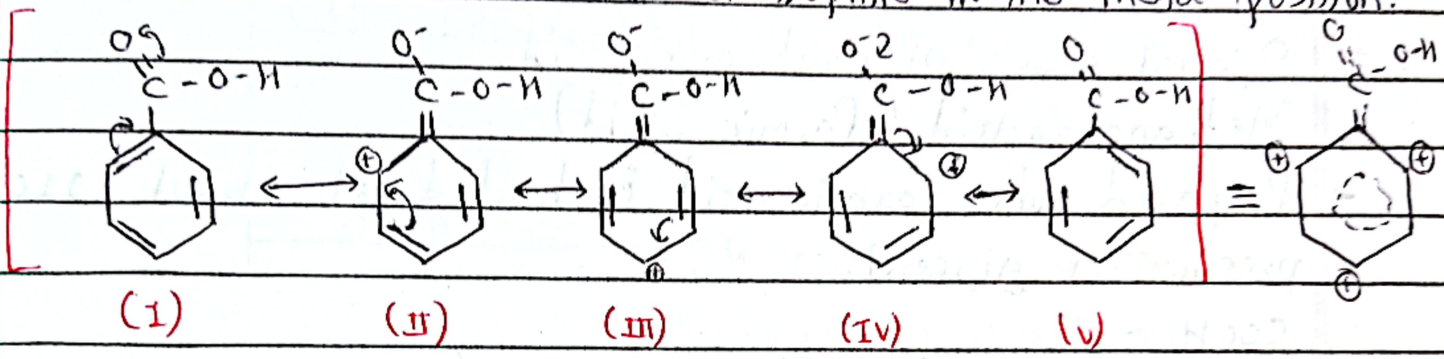
b.# Reaction due to Benzene Ring

→ COOH (carboxyl) group is electron withdrawing group
∴ it withdraws electron from ring.

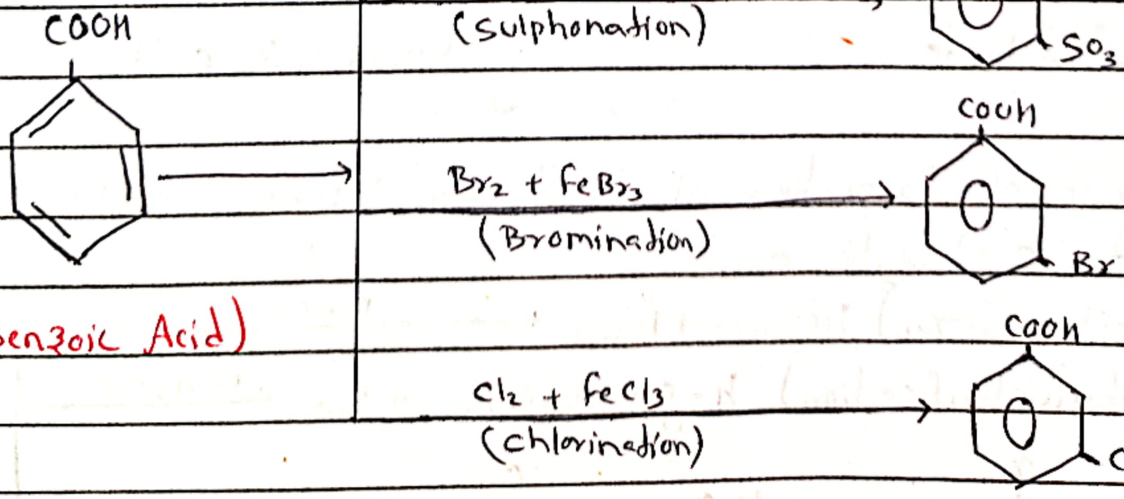
→ After withdrawing +ve charge occurs at 'O' and 'P' position.
∴ e⁻ density increases at 'M' (Meta) position.

Conclusion:

Benzoic Acid substitute the electrophile in the meta position.



Example of electrophilic substitution reaction shown by Benzoic Acid



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Effect of substituent on the acidic strength of carboxylic acid

a. Increasing order of electron donating substituent:

$NH_2 < -OH < OCH_3 < NHCOCH_3 < C_6H_5 < CH_3$ etc.

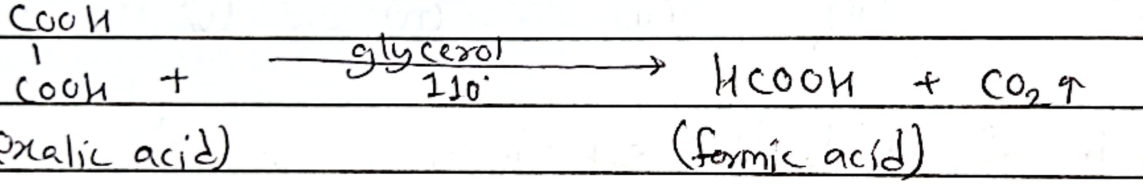
b. ~~Increasing~~ Decreasing order of electron withdrawing substituent:

$-NO_2 > CN > SO_3H > COOH > CHO > COR > X$

Special cases of carboxylic acid

Methanoic Acid (formic Acid)

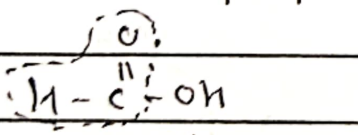
→ Prepared when oxalic acid is heated at about 110°c in the presence of glycerol.



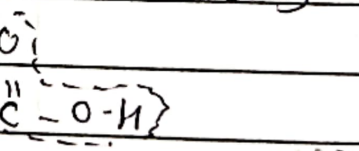
(oxalic acid) (formic acid)

Abnormal behaviour (dual functional nature)

→ show both properties of aldehyde and carboxylic acid.



Aldehyde



Carboxylic acid

Chemical Properties of Methanoic (formic Acid)

As carboxylic acid

(Acid-Base rxn) $HCOONa + H_2O \leftarrow NaOH$

~~Ethyl~~(Esterification) $H-C(=O)-OC_2H_5 + H_2O \leftarrow C_2H_5OH$

$H-C(=O)-NH_2 \xleftarrow[\Delta]{-H_2O} H-C(=O)-ONH_4 \xleftarrow{NH_3} HCOOH$

$HCl + POCl_3 + H-C(=O)-Cl \leftarrow PCl_5$

H-COOH

Tollen's reagent → $2Ag\downarrow + CO_2\uparrow + 2H_2O + 4NH_3\uparrow$

$KMnO_4/H^+$ → $2KMnO_4 + H_2SO_4 \longrightarrow K_2SO_4 + MnSO_4 + 3H_2O + (O)$

$5\,HCOOH + 5(O) \longrightarrow 5\,CO_2 + 5H_2O$

$HCOOH + 2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5\,CO_2\uparrow$

Fehling soln. → $HCOOH + [2Cu^{++} + 4OH^-] \rightarrow CO_2\uparrow + Cu_2O\downarrow + 3H_2O$

$2HgCl_2$ →

(i) $Hg_2Cl_2 + 2HCl + CO_2$

(ii) $Hg_2Cl_2 + Hg_2Cl_2 + HCOOH \longrightarrow 2Hg\downarrow + 2HCl + CO_2$ (grey ppt.)

Extra Reactions:

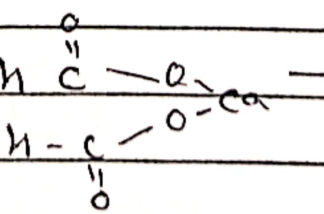
(i) Action of heat at 160°C

$HCOOH \xrightarrow[\Delta]{160^\circ C} H_2\uparrow + CO_2\uparrow$

(ii) Action with conc. H_2SO_4 and P_2O_5

$HCOOH \xrightarrow{conc.\,H_2SO_4} H_2O + CO$

(iii) Heating calcium formate

$HCOOH + Ca \longrightarrow$  $\longrightarrow HCHO + CaCO_3$

$HCOOH$

(iv) Action with soda lime ($NaOH + CaO$)

$HCOOH + NaOH \xrightarrow{CaO} HCOONa + H_2O$

$HCOONa + NaOH \xrightarrow{CaO} Na_2CO_3 + H_2\uparrow$

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Uses of Methanoic Acid (formic Acid)

i. Used as antiseptic and preservatives for fruits.
ii. Used in laboratory preparation of CO.
iii. Used as coegulating agent for latex in rubber industry.

Test for carboxylic Acid

(i) Bicarbonate and carbonate Test:
Produces CO_2 effervescene which turn lime water milky.

(ii) Litmus paper test: Blue to red
(iii) With PCl_3 or $SOCl_2$: evolution of HCl gas
(iv) Esterification test: When react with alcohol (ethanol) in presence of conc. H_2SO_4, ester with sweet smell is obtained.