CARBOXYLIC ACIDS

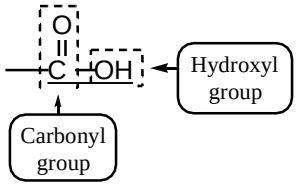
NEB Syllabus:

Aliphatic carboxylic acid:

- *Introduction, nomenclature, examples*
- *Preparation of monocarboxylic acids from*
  a) *Aldehydes*
  b) *Nitriles*
  c) *Grignard regents*
  d) *Dicarboxylic acid*
  e) *Sodium alkoxide*
  f) *Trihaloalkanes*
- *Physical properties of monocarboxylic acids*
- *Chemical properties:*
  a) *Action with alkalies metal oxides*
  b) *Action with metal carbonates*
  c) *Action with metal bicarbonates*
  d) *Action with PCl_3*
  e) *Action with $LiAlH_4$*
  f) *Dehydration of carboxylic acid*
  g) *Esterification*
  h) *Halogenation*
- *Effect of substituent on the acidic strength of carboxylic acid*
- *Laboratory preparation of Methanoic acid*
- *Abnormal behavior of Methanoic acid*
- *Uses of carboxylic acid*

Introduction:

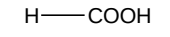
Organic compounds containing carboxyl group (-COOH) as a functional group are called carboxylic acid. The carboxyl is the combination carbonyl & hydroxyl group.



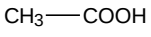
✓ **General representation:** R- COOH or Ar-COOH

Where. R= alkyl groups (in aliphatic carboxylic acids) and Ar = aryl group usually Phenyl group (in aromatic carboxylic acid)

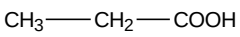
✓ **Examples and Nomenclature of aliphatic carboxylic acids:**



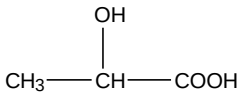
Methanoic acid
(Formic acid)



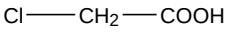
Ethanoic acid
(Acetic acid)



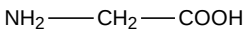
Propanoic acid



2-Hydroxy propanoic acid



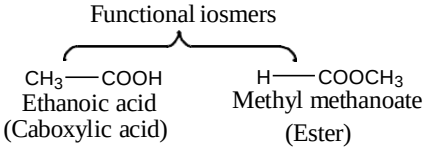
2-Chloro ethanoic acid
(□-Chloroacetic acid)



2-Amino ethanoic acid
(□-aminoacetic acid)

✓ **Isomerism:**

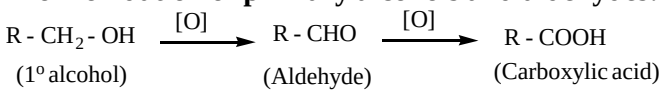
Example: Isomers of $C_2H_4O_2$



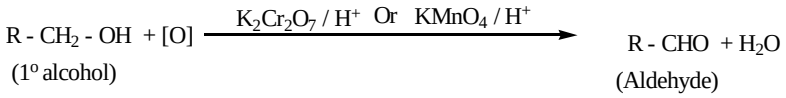
NEB 2070 set D & 070 supp. *Write the functional isomer of ethanoic acid & its IUPAC names.*

✓ **General Methods of Preparation:**

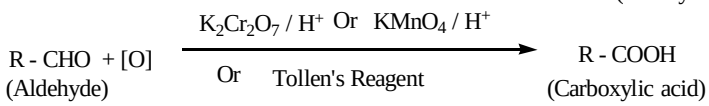
(1) From oxidation of primary alcohols and aldehydes:



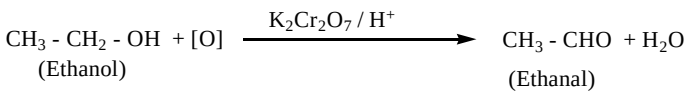
(1° alcohol) (Aldehyde) (Carboxylic acid)



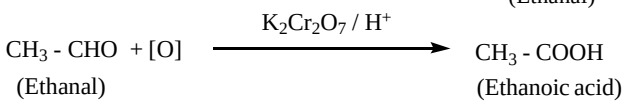
(1° alcohol) (Aldehyde)



(Aldehyde) (Carboxylic acid)

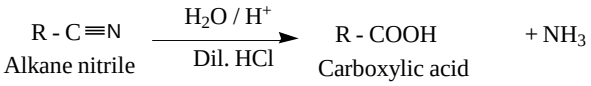


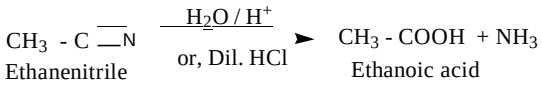
(Ethanol) (Ethanal)



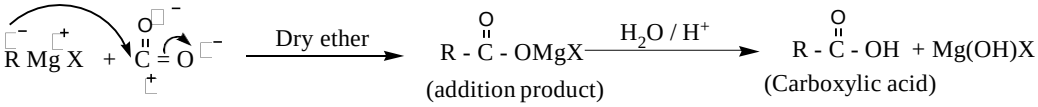
(Ethanal) (Ethanoic acid)

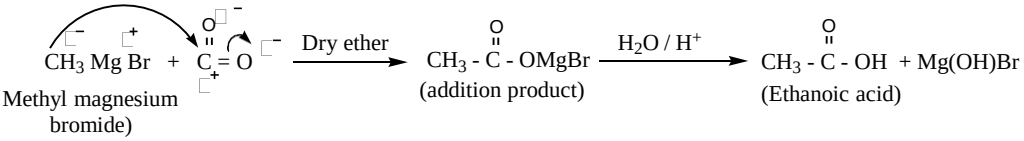
(2) From nitriles (or cyanides) :





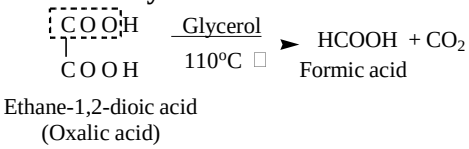
(3) From Grignard's reagent:

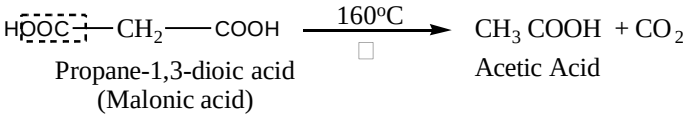




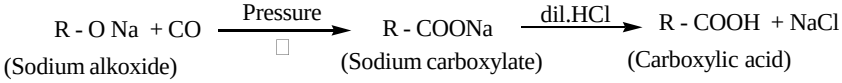
NEB 2074 set A & set B , 2071 set D : *What is meant by carboxylation reaction? Write an example of it.*

(4) From dicarboxylic acid:



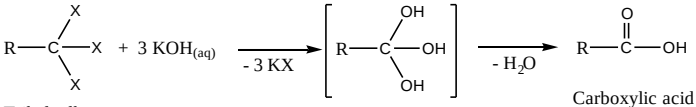


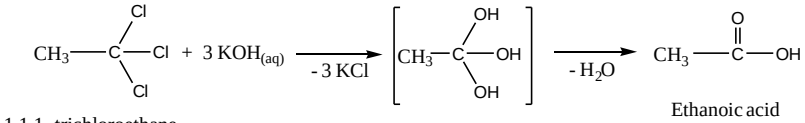
(5) From sodium alkoxide:

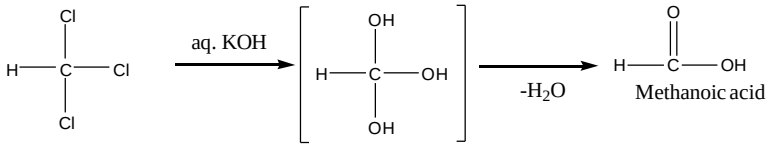


NEB 2072 set C *Give the chemical reaction for the preparation of ethanoic acid from i) sodium methoxide ii) ethane nitrile iii) methyl magnesium iodide*

(6) From Trihaloalkanes:



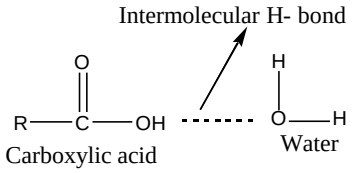




NEB 2071 supp Q 31 a, set D . *How would you prepare ethanoic acid from i) Tribromoethane ii) ethane nitrile iii) Methyl magnesium iodide*
NEB 2074 set B . *How would you prepare ethanoic acid from i) 1,1,1-Trichloroethane ii) ethane nitrile iii) Methyl magnesium iodide ?*

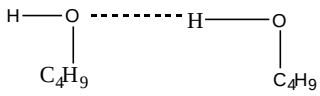
Physical Properties

a)State, color and odor: Lower members of carboxylic acids up to C_{10} are colorless unpleasant smelling liquid while higher members are colorless, odorless waxy solid,
b)Solubility: The first four members completely soluble in water because they can form intermolecular hydrogen bond with water molecule whereas higher members are insoluble in water due to increase in hydrophobic nature of hydrocarbon portion.



c) Boiling point:
Carboxylic acids have higher boiling point than alcohol, ether etc. of comparable molecular mass because carboxylic acid can form two H- bonds & gives stable cyclic dimeric structure whereas alcohol can form only one H- bond with each other & ether cannot form such H-bonds with themselves.
Example:

Acetic acid	Butanol	Ethoxyethane
CH_3COOH	$CH_3CH_2CH_2CH_2OH$	$CH_3CH_2\,O\,CH_2CH_3$
MW= 74	MW= 74	MW= 74
B.pt= 141°C	B.pt= 118°C	B.pt= 34.6°C



NEB 2064 Q **7** *The boiling point of Methanoic acid is higher than ethanol though they have same molecular mass explain.*

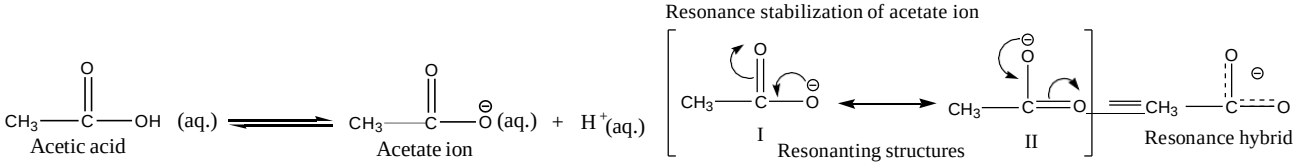
Boiling increases with the increase in molecular mass in homologous series of carboxylic acid due to increase in size and strength of force held between the molecules.

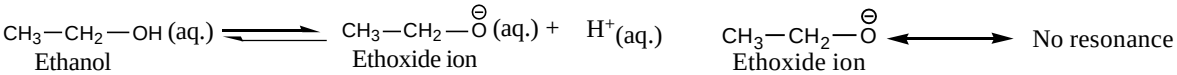
Example: $HCOOH < CH_3COOH < CH_3CH_2COOH$

Chemical Properties:

1) Reaction due to H – atom of the – COOH group : Acidic nature

Carboxylic acids are more acidic in nature than aliphatic alcohols because the carboxylate ion formed after the ionization of carboxylic acid is resonance stabilized whereas alkoxide ion formed after the ionization of alcohol is not resonance stabilized. More the stability of ion in aqueous solution higher will be the acid strength.
Example: Acetic acid (ethanoic acid or acetic acid is stronger acid than ethanol)

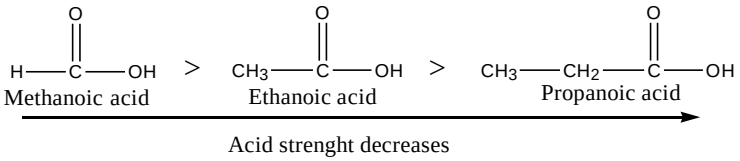




Effect of substituent on acidity of carboxylic acid:

i) Electron donating groups (+I groups such as CH_3-, OH, NH_2 etc) donates the electrons, destabilize the carboxylate anion by intensifying the negative charge & decrease the acid strength of carboxylic acid.

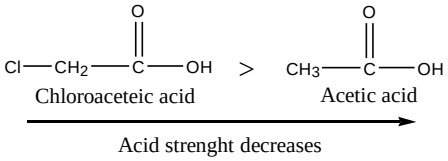
Example:



NEB 2070 set C , 2072 set E,058 *Why is ethanoic acid weaker acid than Methanoic acid ?*

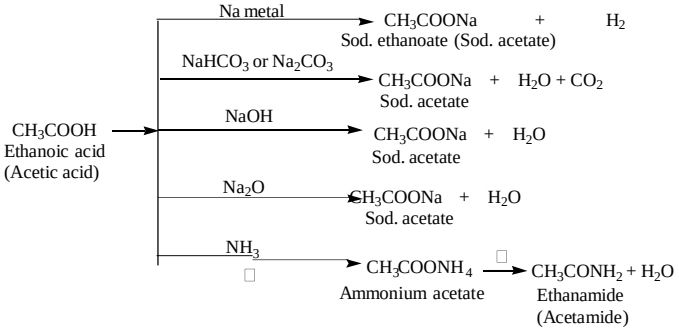
ii) Electron withdrawing groups (-I groups such as F, Cl, Br, I, CN, NO_2 etc) withdraws the electrons, stabilize the carboxylate anion by dispersing the negative charge & increase the acid strength of carboxylic acid.

Example:



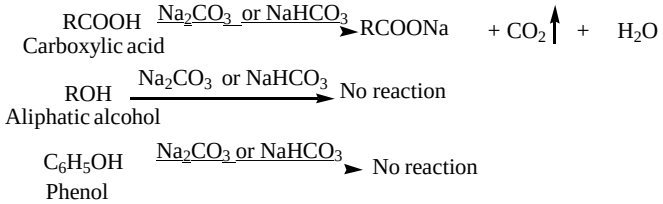
NEB 2073 set D, 059, *Why is Chloroacetic acid stronger acid than acetic acid?*

Reactions to show the acidic nature of carboxylic acid

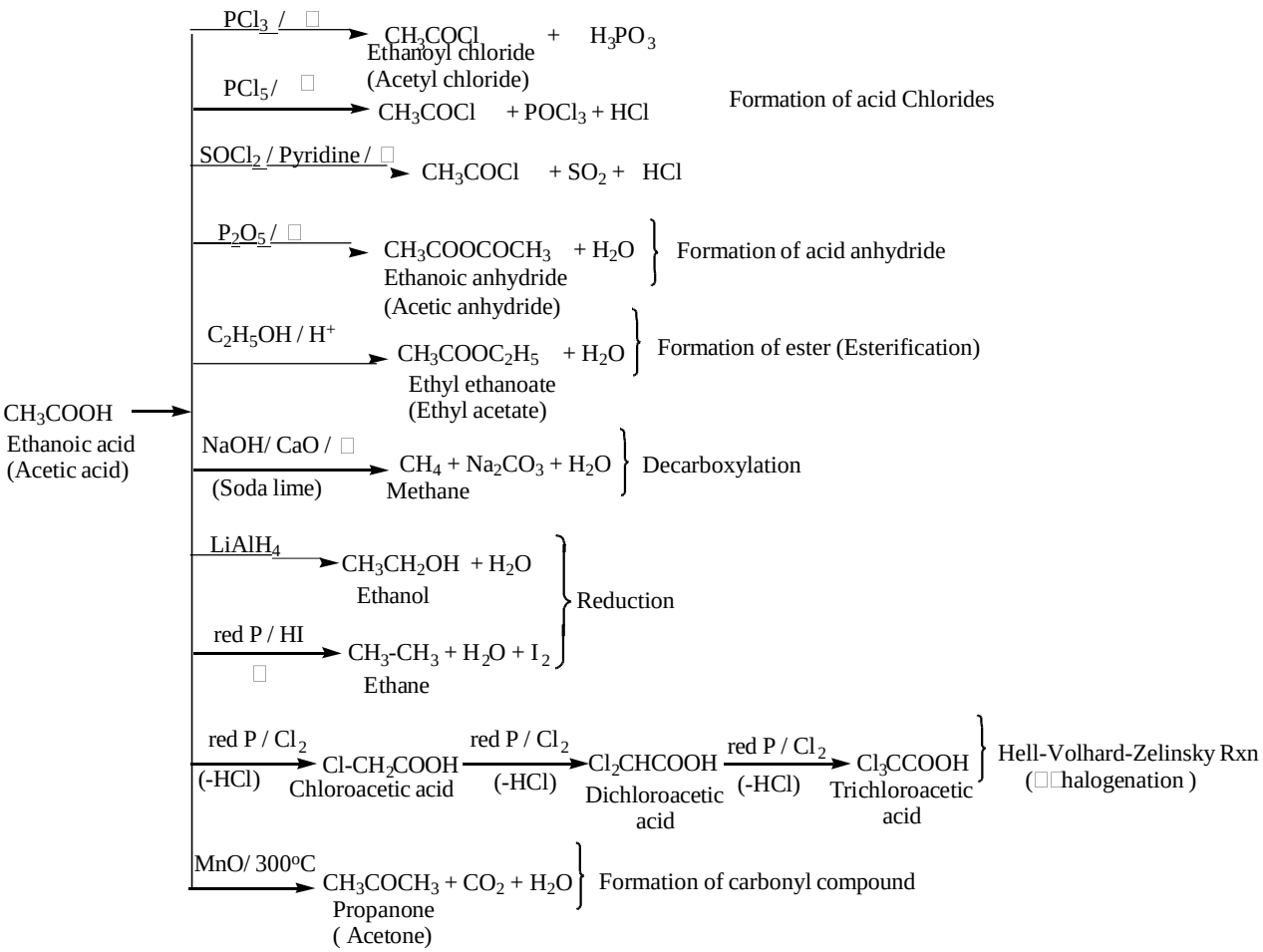


Laboratory Test of Carboxylic acid:

Carboxylic acid reacts with sodium carbonate or sodium bicarbonate & produce brisk effervescence of carbon dioxide gas whereas other weak acids like alcohol & phenols does not reacts with sodium carbonate or sodium bicarbonate.



Other Important reactions:



NEB 2069 set A: *Write an example of Decarboxylation reaction.*

NEB 2071 supp: *What happens when ethanoic acid is heated with i) P_2O_5 ii) Alcohol in presence of H_2SO_4?*

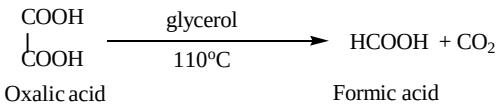
NEB 2069 supp. Set B: *How does ethanoic acid reacts with i) ethanol ii) PCl_5 ?*

NEB 2061, 2070: *What products are obtained when CH_3COOH is allowed to reacts with a) NaOH b) NaOH/CaO c) PCl_5 d) P_2O_5 e) $LiAlH_4$ f) $SOCl_2$ (NEB 2071 supp) g) HI in presence of red Phosphorous h) passed over heated MnO i) warmed with ethanol in presence of conc. H_2SO_4?*

NEB 2071, 2066 Set C: *Write the suitable chemical reaction to convert ethanoic acid into a) methane b) Methyl ethanoate c) ethanoic anhydride*

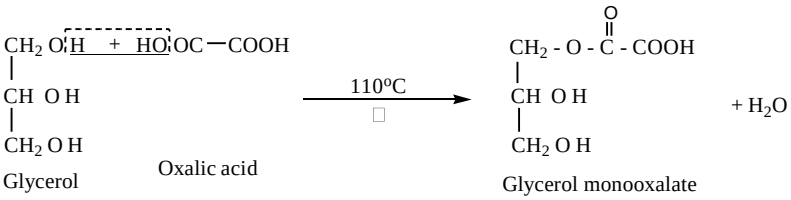
Laboratory Preparation of Methanoic acid (Formic acid)

Principle:

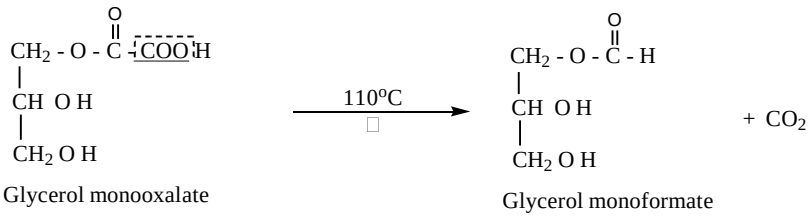


Actually, it completes in three steps, glycerol acts as a catalyst.

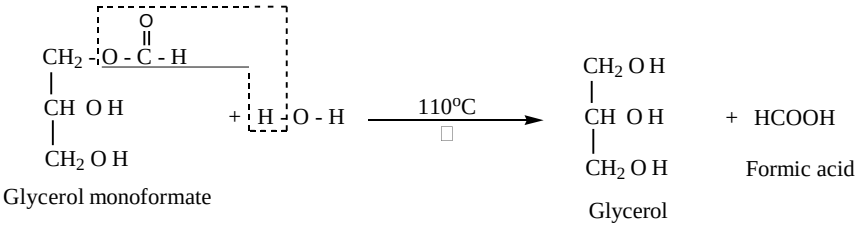
Step 1: Formation of glycerol mono oxalate



Step 2: Formation of glycerol mono formate.



Step 3: Formation of formic acid



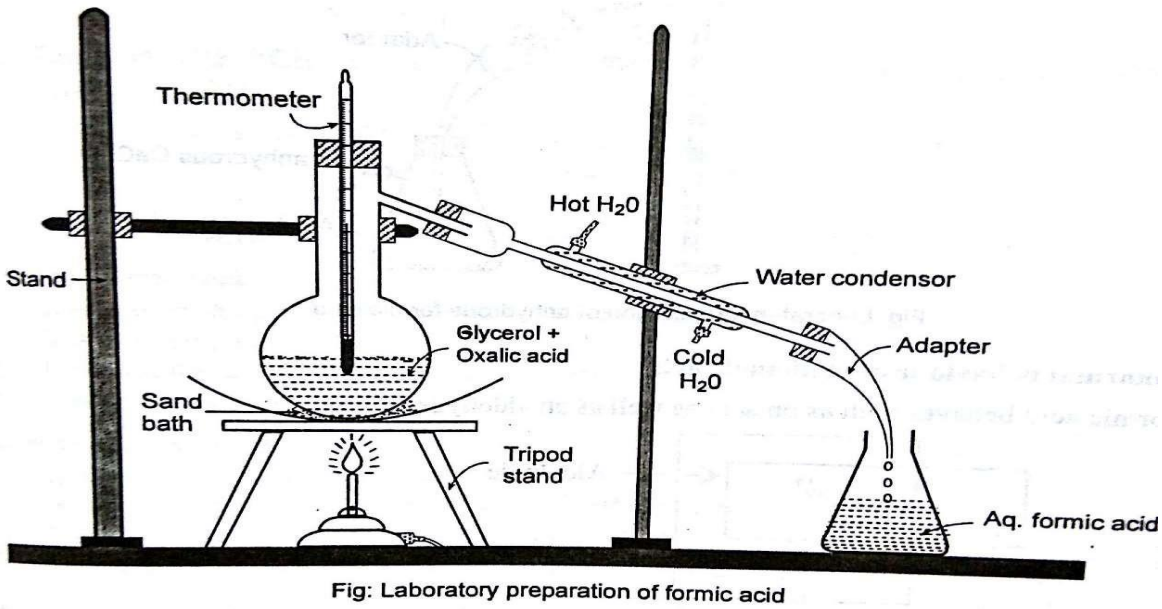


Fig: Laboratory preparation of formic acid

Procedure:

40 gram crystalline oxalic acid + 50 gram anhydrous glycerol are taken in distillation flask fitted with thermometer and water condenser. Then the flask is heated about 110°C till the evolution of CO_2. Now the flask is cooled and a fresh 40 gram crystalline oxalic acid is added. The mixture is again heated to 110°C, the aqueous solution of formic acid collects in receiver.

Preparation of Anhydrous Formic acid from aqueous formic acid

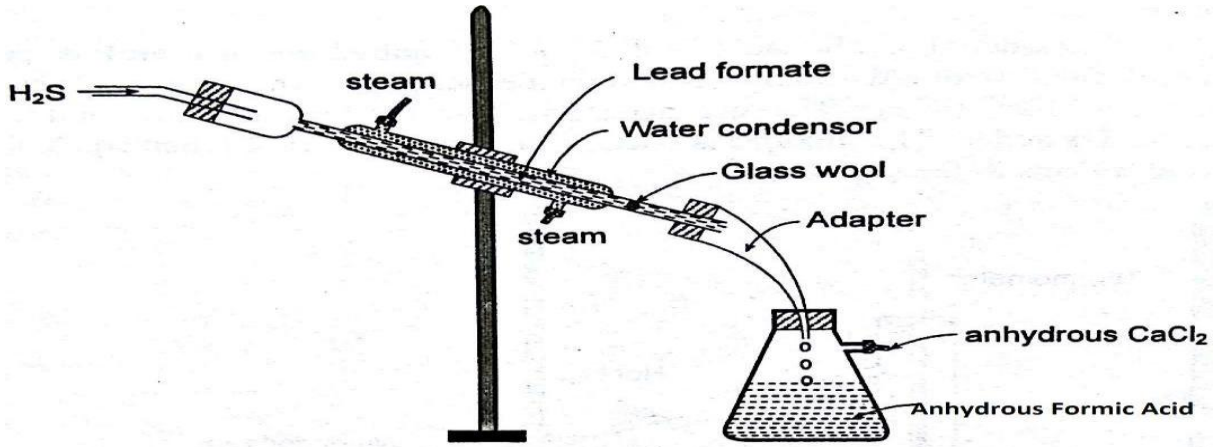


Fig: Laboratory preparation of anhydrous formic acid

The aq HCOOH is treated with $PbCO_3$ to get lead formate, $(HCOO)_2Pb$, which is filtered and concentrated to get crystal of $(HCOO)_2Pb$

$$2HCOOH + PbCO_3 \longrightarrow \underset{\text{Lead formate}}{(HCOO)_2Pb} + H_2O + CO_2$$

$$(HCOO)_2Pb\ (aq) \xrightarrow{\text{Crystallization}} (HCOO)_2Pb$$

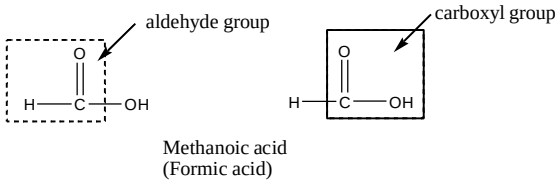
The $(HCOO)_2Pb$ crystals are packed in inner side of water condenser and H_2S gas is allowed to pass through the inner tube to get anhydrous formic acid. While steam is passed through its outer jacket.

$$(HCOO)_2Pb + H_2S \longrightarrow \underset{\text{Formic acid}}{2\ HCOOH} + PbS$$

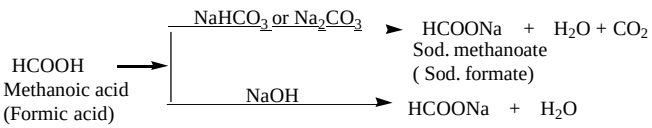
NEB 2073, 2071, 2070, 2065, 2067, 2064, 2057 describe the laboratory preparation of anhydrous Methanoic acid or formic acid form hydrous or aq. Formic acid. (5)

Important reactions of formic acid

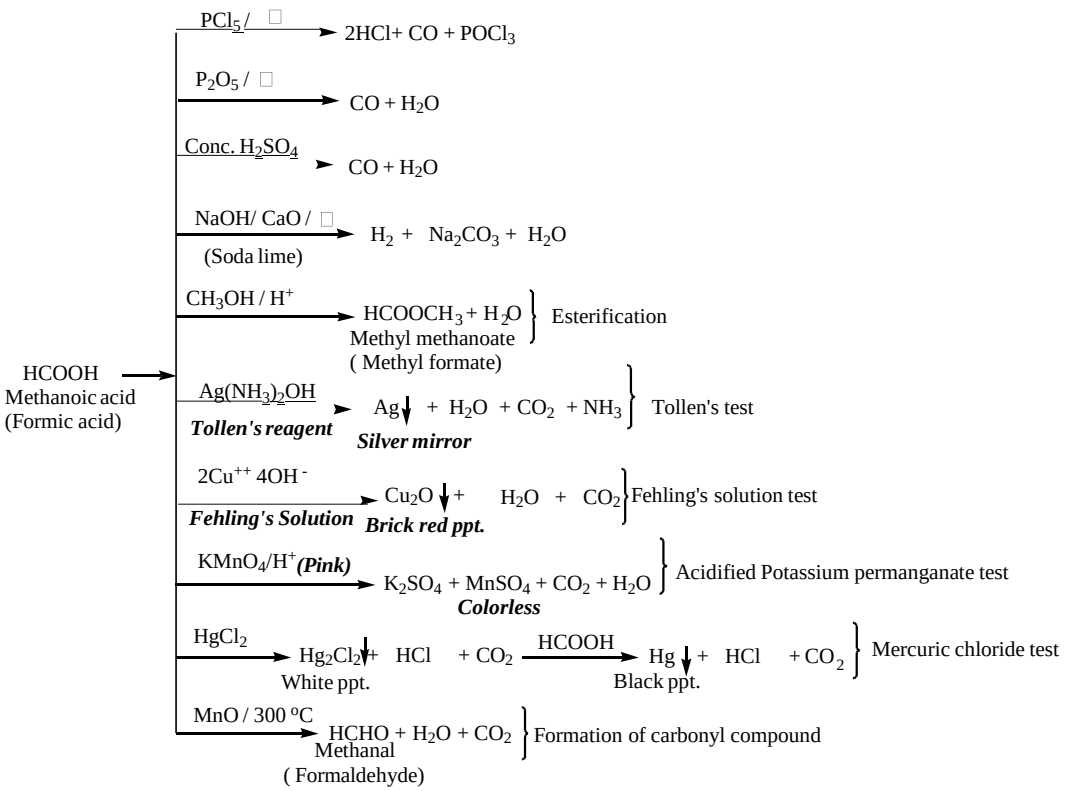
Formic acid differs from other carboxylic acid because it contains both carboxyl group (-COOH) and aldehyde (-CHO) group. So it behaves as both acid and aldehyde.



Acidic Nature:



Abnormal behavior of Methanoic acid or formic acid:



Difference in between properties of HCOOH & CH_3COOH

HCOOH	CH_3COOH
1. Gives positive Tollen's test	1. Does not gives positive Tollen's test
2. Gives positive Fehling solution test	2. Does not give positive Fehling solution test
3. Reacts with acidified $KMnO_4$	3. Does not reacts with acidified $KMnO_4$
4. Gives CO & H_2O When heated with P_2O_5	4. Gives ethanoic anhydride or acetic anhydride when heated with P_2O_5
5. Gives CO & H_2O when reacts with conc. H_2SO_4	5. Does not reacts with conc. H_2SO_4

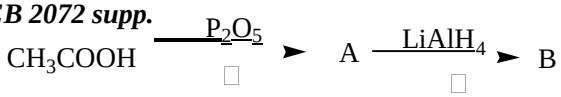
USES:

1. Formic acid is used in leather tanning, textile industry for dying process, prepn of carbon monoxide, as medicine for treatment of gout.
2. Acetic acid is used in plastic and rubber industries, as coagulant in manufacture of rubber from latex and casein from milk, as vinegar, as solvent.

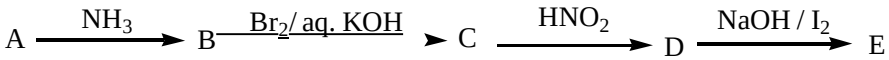
NEB 2071 Set C, 2065, 2060 *Write a chemical test to distinguish ethanoic acid from Methanoic acid.*
NEB 2069 *Methanoic acid gives Tollen's test but ethanoic acid does not. Give reason.*
NEB 2072 Set E *How is ethanoic acid distinguished from Methanoic acid ?*
NEB 2063 *What happens when Methanoic acid is warmed with Ammoniacal silver nitrate ?*
NEB 2062, 2072 *How would you convert Methanoic acid into ethanoic acid and vice versa?*

Some organic conversion questions

NEB 2072 supp.

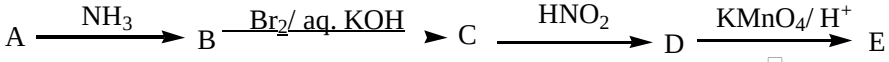


NEB 2070



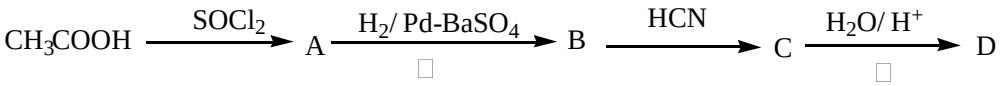
Compound E produce ethyne when heated with silver powder.

NEB 2069

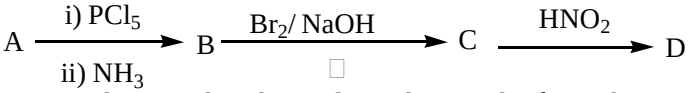


Compound E can be obtained by heating oxalic acid in presence of gylcerol.

NEB 2068

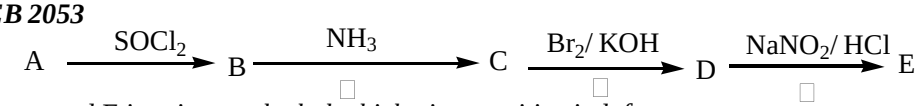


NEB 2057



Compound A is carboxylic acid & calcium salt of A on heating gives acetone.

NEB 2053



Compound E is primary alcohol which gives positive iodoform test.