

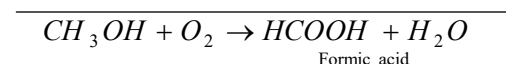
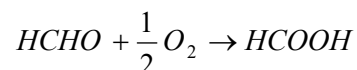
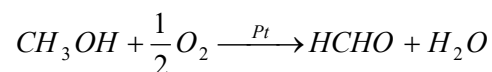
Individual members of Monocarboxylic acids

Formic Acid or Methanoic acid (HCOOH)

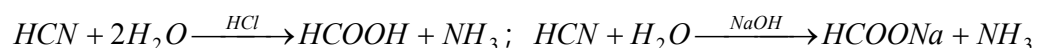
Formic acid is the first member of monocarboxylic acids series. It occurs in the sting of bees, wasps, red ants, stinging nettles. and fruits. In traces it is present in perspiration, urine, blood and in caterpillars.

(1) **Methods of preparation:** The following methods can be used for its preparation

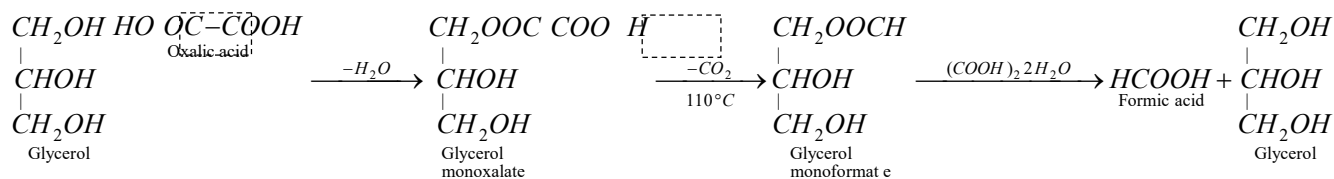
(i) **Oxidation of methyl alcohol or formaldehyde:**



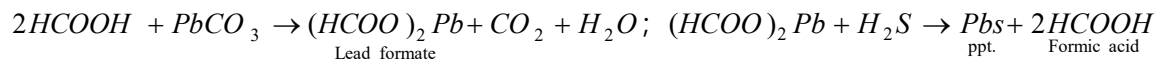
(ii) **Hydrolysis of hydrocyanic acid:** Formic acid is formed by the hydrolysis of HCN with acids or alkalies.



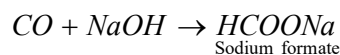
(iii) **Laboratory preparation:** Formic acid is conveniently prepared in the laboratory by heating glycerol with oxalic acid at 100-120°C. In actual practice, glycerol is first heated at 105 °C and then hydrated oxalic acid is added and the temperature is raised to 110°C. Glycerol monoxalate is first formed which decomposes into glycerol monoformate and carbon dioxide. When the evolution of carbon dioxide ceases, more of oxalic acid is added. The monoformate gets hydrolysed to formic acid regenerating glycerol which reacts with fresh oxalic acid. Thus, a small quantity of glycerol is sufficient to convert large quantities of oxalic acid into formic acid.



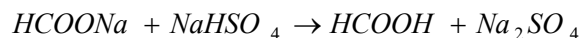
The following procedure is applied for obtaining anhydrous formic acid.



(iv) **Industrial preparation:** Formic acid is prepared on industrial scale by heating sodium hydroxide with carbon monoxide at 210°C under a pressure of about 10 atmospheres.

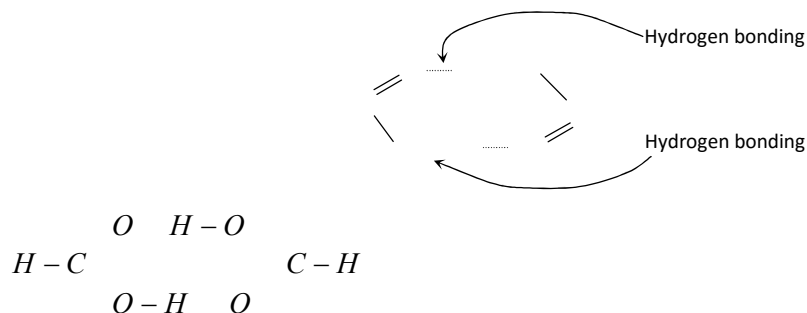


Sodium formate thus formed is distilled with sodium hydrogen sulphate, when anhydrous formic acid distils over.

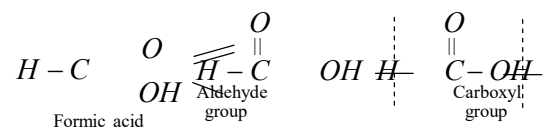


(2) Physical properties

- (i) It is a colourless pungent smelling liquid.
- (ii) It melts at 8.4°C and boils at 100.5°C.
- (iii) It is miscible with water, alcohol and ether. It forms azeotropic mixture with water.
- (iv) It is strongly corrosive and causes blisters on skin.
- (v) It exists in aqueous solution as a dimer involving hydrogen bonding.

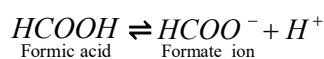


(3) **Chemical properties:** Formic acid is the strongest acid among all the members of the homologous series. It exhibits some characteristics which are not shown by other members. This unique nature is due to the fact that it contains both aldehyde group and carboxyl group.

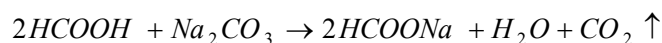
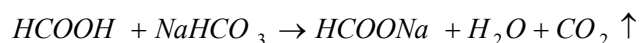


(i) **Acidic properties**

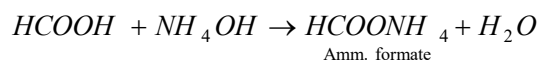
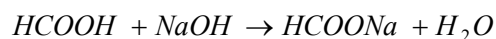
(a) It is a monobasic acid. Its dissociation constant value is 18×10^{-5} at 25°C . Its acidic properties are due to its ionisation in aqueous solution.



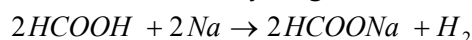
(b) It reacts with carbonates and bicarbonates evolving carbon dioxide.



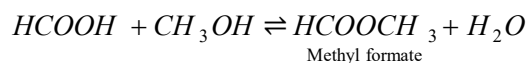
(c) It reacts with alkalis to form corresponding salts. The salts of formic acid are termed as formates. Most of the formates are soluble in water but lead and silver formates are insoluble.



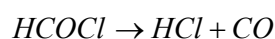
(d) Highly electropositive metals evolve hydrogen when react with formic acid.



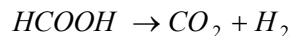
(e) It combines with alcohols to form esters. It is not necessary to use a mineral acid as to catalyse the reaction since the formic acid itself acts as a catalyst.



(f) It reacts with PCl_5 or SOCl_2 to give formyl chloride which is not a stable compound. It decomposes at once into hydrogen chloride and carbon monoxide.

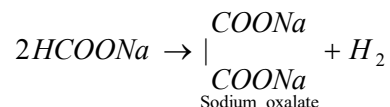


(ii) **Action of heat:** When heated above 160°C , it decomposes to give carbon dioxide and hydrogen.

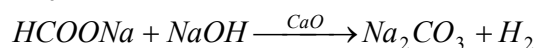


(iii) **Action of heat on formates**

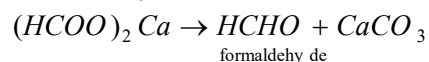
(a) When sodium formate is heated to 360°C. It decomposes to form sodium oxalate and hydrogen.



(b) It does not form a hydrogen when sodium formate is heated with sodalime or its aqueous solution is electrolysed.

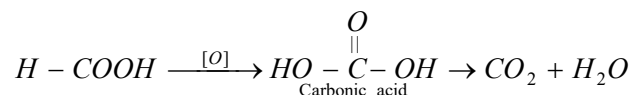


(c) Formaldehyde is formed when dry calcium formate is heated.

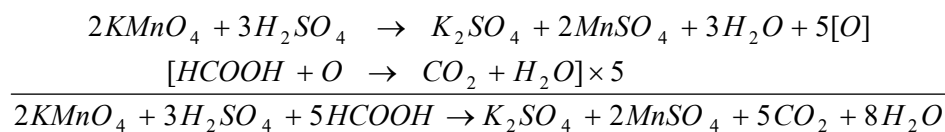


(iv) **Reducing properties**

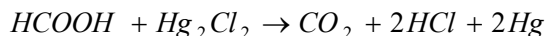
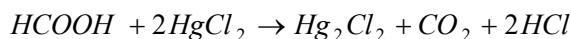
(a) Like aldehyde formic acid behaves as reducing agents, it is oxidised to an unstable acid, carbonic acid, which decompose into CO₂ and H₂O



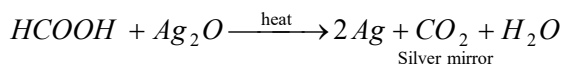
(b) It decolourises acidified KMnO₄.



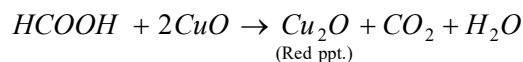
(c) It reduces mercuric chloride to mercurous chloride to mercury black



(d) It reduces ammonical silver nitrate (Tollen reagents)



(e) It reduces fehling solution give red precipitate of Cu₂O

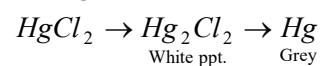


(4) **Uses:** Formic acid is used.

- (i) In the laboratory for preparation of carbon monoxide.
- (ii) In the preservation of fruits.
- (iii) In textile dyeing and finishing.
- (iv) In leather tanning.
- (v) As coagulating agent for rubber latex.
- (vi) As an antiseptic and in the treatment of gout.
- (vii) In the manufacture of plastics, water proofing compounds.
- (viii) In electroplating to give proper deposit of metals.
- (ix) In the preparation of nickel formate which is used as a catalyst in the hydrogenation of oils.
- (x) As a reducing agent.
- (xi) In the manufacture of oxalic acid.

(5) **Tests of Formic Acid**

- (i) It turns blue litmus red.
- (ii) Its aqueous solution gives effervescences with sodium bicarbonate.
- (iii) Its neutral solution gives red precipitate with Fehling's solution.
- (iv) Its neutral solution with Tollen's reagent gives silver mirror or black precipitate.
- (v) It gives white precipitate with mercuric chloride which changes to grey.

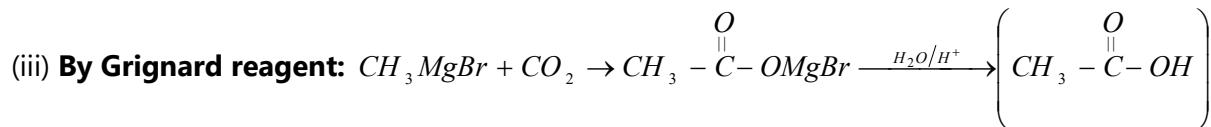


Acetic Acid (Ethanoic Acid) (CH₃COOH)

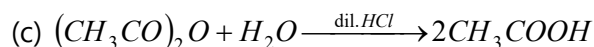
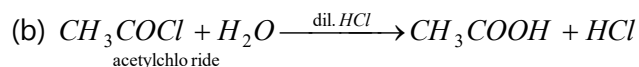
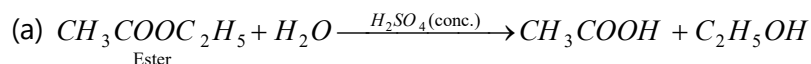
Acetic acid is the oldest known fatty acid. It is the chief constituent of vinegar and hence its name (Latin acetum = vinegar)

(1) **Preparation**



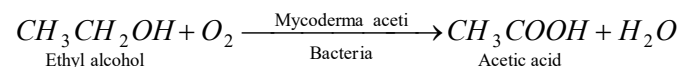


(iv) **By hydrolysis of acetyl chloride, acetic anhydride or acetamide and ester**



(v) **Manufacture of acetic acid**

(a) From ethyl alcohol (Quick vinegar process): Vinegar is 6-10% aqueous solution of acetic acid. It is obtained by fermentation of liquors containing 12 to 15% ethyl alcohol. Fermentation is done by Bacterium *Mycoderma aceti* in presence of air at 30-35°C. The process is termed **acetous fermentation**.



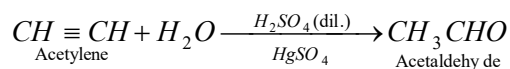
It is a slow process and takes about 8 to 10 days for completion.

In this process, the following precautions are necessary:

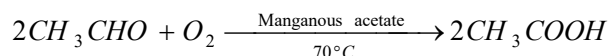
- The concentration of the ethyl alcohol should not be more than 15%, otherwise the bacteria becomes inactive.
- The supply of air should be regulated. With less air the oxidation takes place only up to acetaldehyde stage while with excess of air, the acid is oxidized to CO₂ and water.
- The flow of alcohol is so regulated that temperature does not exceed 35°C which is the optimum temperature for bacterial growth.

Acetic acid can be obtained from vinegar with the help of lime. The calcium acetate crystallized from the solution is distilled with concentrated sulphuric acid when pure acetic acid distils over.

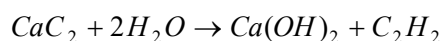
(b) From acetylene: Acetylene is first converted into acetaldehyde by passing through 40% sulphuric acid at 60°C in presence of 1% HgSO₄ (catalyst).



The acetaldehyde is oxidized to acetic acid by passing a mixture of acetaldehyde vapours and air over manganous acetate at 70°C.

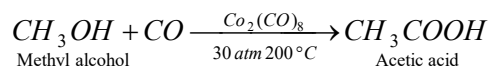


Note: Acetylene required for this purpose is obtained by action of water on calcium carbide.



The yield is very good and the strength of acid prepared is 97%. The method is also quite cheap.

(c) By the action of CO on methyl alcohol : Methyl alcohol and carbon monoxide react together under a pressure of 30 atmospheres and 200°C in presence of a catalyst cobalt octacarbonyl, $Co_2(CO)_8$ to form acetic acid.



(2) Physical properties

(i) At ordinary temperature, acetic acid is a colorless, corrosive liquid with a sharp pungent odour of vinegar. It has a sour taste.

(ii) Below 16.5°C, it solidifies as an icy mass, hence it is named glacial acetic acid.

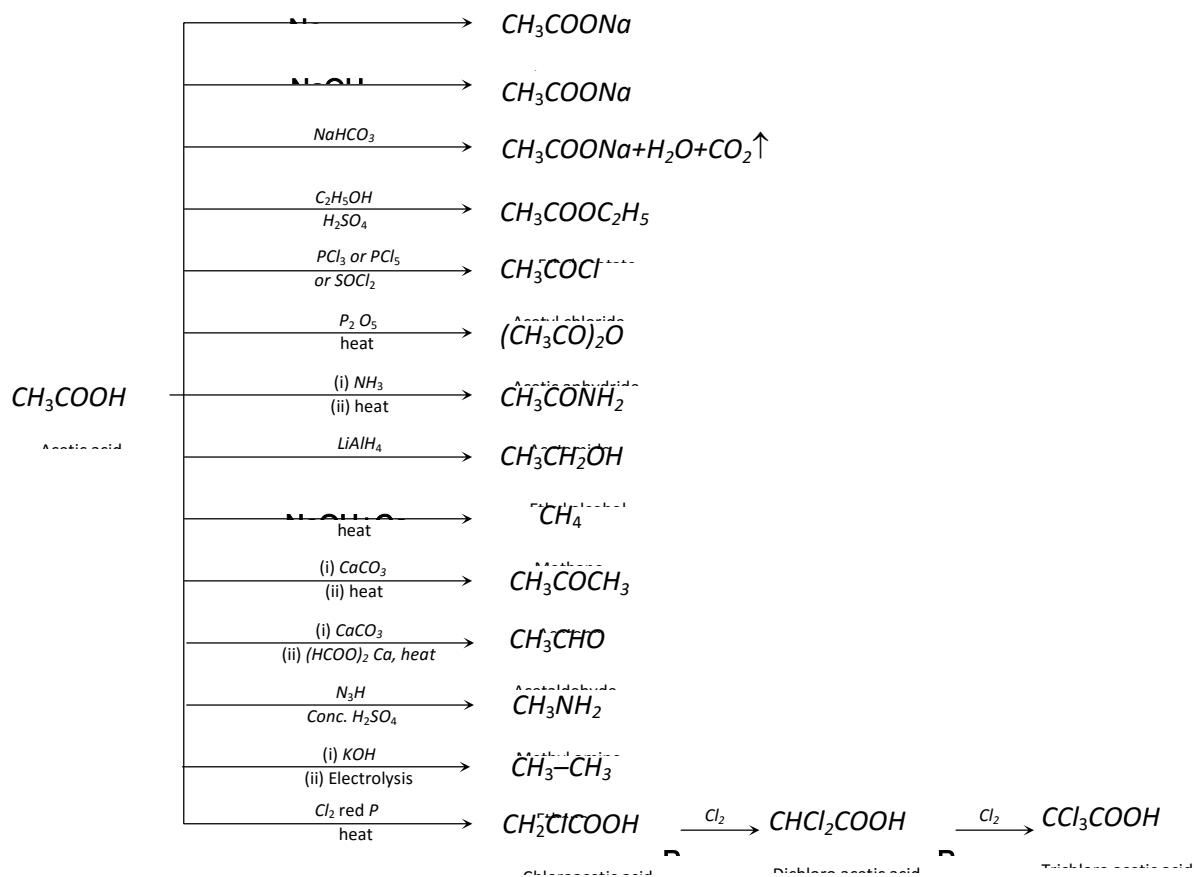
(iii) It boils at 118°C. The high boiling point of acetic acid in comparison to alkanes, alkyl halides or alcohols of nearly same molecular masses is due to more stronger hydrogen bonding between acid molecules. This also explains dimer formation of acetic acid in vapours state.

(iv) It is miscible with water, alcohol and ether in all proportions.

(v) It is good solvent for phosphorus, sulphur, iodine and many organic compounds.

(3) **Chemical properties:** Acetic acid is a typical member of fatty acids. It shows all the general characteristics of monocarboxylic acids.

Reaction chart of Acetic acid



(4) **Uses:** It is used,

(i) As a solvent and a laboratory reagent.

(ii) As vinegar for table purpose and for manufacturing pickles.

(iii) In coagulation of rubber latex.

(iv) For making various organic compounds such as acetone, acetic anhydride, acetyl chloride, acetamide and esters.

(v) For making various useful metallic acetates, such as:

- (a) Basic copper acetate which is used for making green paints.
- (b) Al, Fe and Cr acetates which are used as mordants in dyeing.
- (c) Lead tetra-acetate which is a good oxidising agent.
- (d) Basic lead acetate which is used in the manufacture of white lead.
- (e) Aluminium acetate which is used in the manufacture of water-proof fabrics.
- (f) Alkali acetates which are used as diuretics.

(5) Tests

- (i) Its aqueous solution turns blue litmus red.
- (ii) Its aqueous solution gives effervescences with sodium bicarbonate.
- (iii) The neutral solution of the acetic acid gives a wine red colour with neutral ferric chloride solution.
- (iv) When heated with ethyl alcohol in presence of a small amount of concentrated sulphuric acid, it forms ethyl acetate which has fruity smell.
- (v) Acetic acid does not show reducing properties like formic acid, i.e., it does not reduce Tollen's reagent, Fehling's solution and mercuric chloride.

Comparison of Formic Acid and Acetic Acid

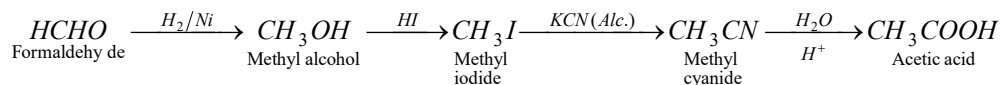
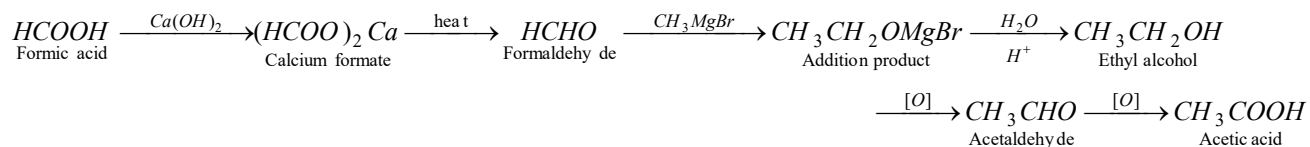
Property	Formic acid	Acetic acid
1. Acidic nature, (i) With electro-positive metals	Forms salts, Hydrogen is evolved. $HCOOH + Na \rightarrow HCOONa + \frac{1}{2} H_2$	Forms salts. Hydrogen is evolved. $CH_3COOH + Na \rightarrow CH_3COONa + \frac{1}{2} H_2$
(ii) With bases	Forms salts. $HCOOH + NaOH \rightarrow HCOONa + H_2O$	Forms salts. $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

(iii) With carbonates and bicarbonates	Forms salts. Carbon dioxide is evolved. $HCOOH + NaHCO_3 \rightarrow HCOONa + H_2O + CO_2$	Forms salts. Carbon dioxide is evolved. $CH_3COOH + NaHCO_3 \rightarrow$ $CH_3COONa + H_2O + CO_2$
2. Ester formation	Forms esters when treated with alcohols. $HCOOH + C_2H_5OH \rightarrow HCOOC_2H_5 + H_2O$	Forms esters when treated with alcohols. $CH_3COOH + C_2H_5OH \xrightarrow{H_2SO_4(conc.)}$ $CH_3COOC_2H_5 + H_2O$
3. Reaction with PCl_5	Forms formyl chloride which decomposes into CO and HCl. $HCOOH + PCl_5 \rightarrow HCOCl(HCl + CO) + POCl_3 + HCl$	Forms acetyl chloride which is a stable compound. $CH_3COOH + PCl_5 \rightarrow$ $CH_3COCl + POCl_3 + HCl$
4. Heating of ammonium salt	Forms formamide. $HCOONH_4 \rightarrow HCONH_2 + H_2O$	Forms acetamide. $CH_3COONH_4 \rightarrow CH_3CONH_2 + H_2O$
5. Heating alone	it decomposes into CO_2 and H_2 $HCOOH \rightarrow CO_2 + H_2$	Unaffected
6. Heating with conc. H_2SO_4	Decomposed into CO and H_2O $HCOOH \xrightarrow[H_2SO_4]{Conc.} CO + H_2O$	Unaffected
7. Reaction with Cl_2 in presence of red P	Unaffected	Forms mono, di or trichloro acetic acids.
8 Action of heat on salts, (i) Calcium salt	Forms formaldehyde. $(HCOO)_2Ca \rightarrow HCHO + CaCO_3$	Forms acetone. $(CH_3COO)_2Ca \rightarrow CH_3COCH_3 + CaCO_3$
(ii) Sodium salt	Forms sodium oxalate. $2HCOONa \xrightarrow{heat} \begin{array}{c} COONa \\ \\ COONa \end{array} + H_2$	Unaffected.
(iii) Sodium salt with soda-lime	Forms sodium carbonate and H_2 . $HCOONa + NaOH \xrightarrow{CaO} Na_2CO_3 + H_2$	Forms sodium carbonate and methane. $CH_3COONa + NaOH \xrightarrow{CaO}$ $CH_4 + Na_2CO_3$
9. Electrolysis of sodium or potassium salt	It evolves hydrogen.	It forms ethane.
10. On heating with P_2O_5	Unaffected	Forms acetic anhydride.

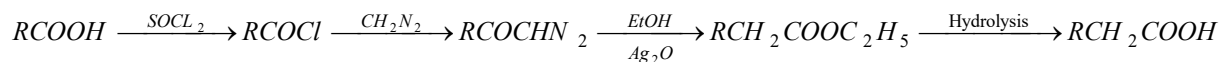
		$2CH_3COOH \xrightarrow{P_2O_5} (CH_3CO)_2O + H_2O$
11. Reducing nature, (i) Tollen's reagent	Gives silver mirror or black precipitate. $HCOOH + Ag_2O \rightarrow 2Ag + CO_2 + H_2O$	Unaffected.
(ii) Fehling's solution	Gives red precipitate $HCOOH + 2CuO \rightarrow Cu_2O + CO_2 + H_2O$	Unaffected.
(iii) Mercuric chloride	Forms a white ppt. which changes to greyish black. $HgCl_2 \rightarrow Hg_2Cl_2 \rightarrow 2Hg$	Unaffected.
(iv) Acidified $KMnO_4$	Decolourises	Unaffected.
12 Acid (neutral solution) + $NaHSO_3$ + Sodium nitroprusside.	Greenish blue colour.	Unaffected.
13 Acid (neutral solution) + neutral ferric chloride	Red colour which changes to brown ppt. on heating.	Wine red colour.

Interconversions

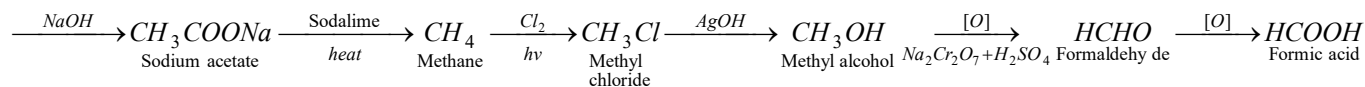
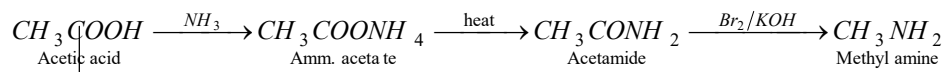
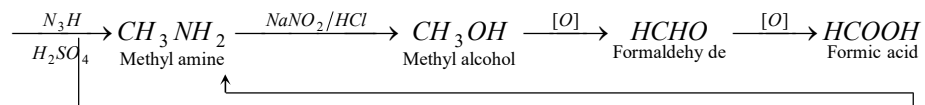
(1) **Ascent of series:** Conversion of formic acid into acetic acid.



Arndt-Eistert homologation: This is a convenient method of converting an acid, RCOOH to RCH₂COOH.



(2) **Descent of series:** Conversion of acetic acid into formic acid.



Conversion of Acetic acid into other organic compound

