



(ii) It is extremely soluble in water. Its solubility in water may be due to hydrogen bonding between water molecules and its hydrate.

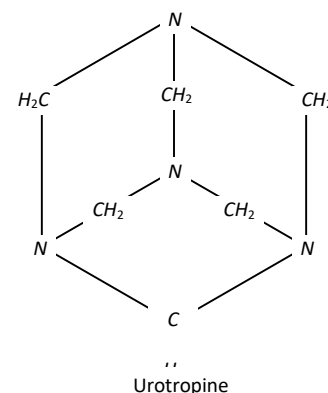
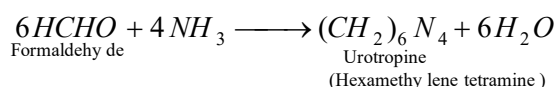
(iii) It can easily be condensed into liquid. The liquid formaldehyde boils at  $-21^{\circ}\text{C}$ .

(iv) It causes irritation to skin, eyes, nose and throat.

(v) Its solution acts as antiseptic and disinfectant.

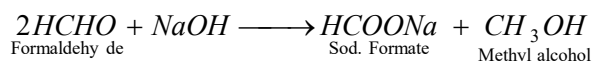
(3) **Chemical properties:** Formaldehyde is structurally different from other aldehydes as it contains no alkyl group in the molecule. Though it shows general properties of aldehydes, it differs in certain respects. The abnormal properties of formaldehyde are given below

(i) **Reaction with ammonia:** Like other aldehydes, formaldehyde does not form addition product but a crystalline compound, hexamethylenetetramine, with ammonia.



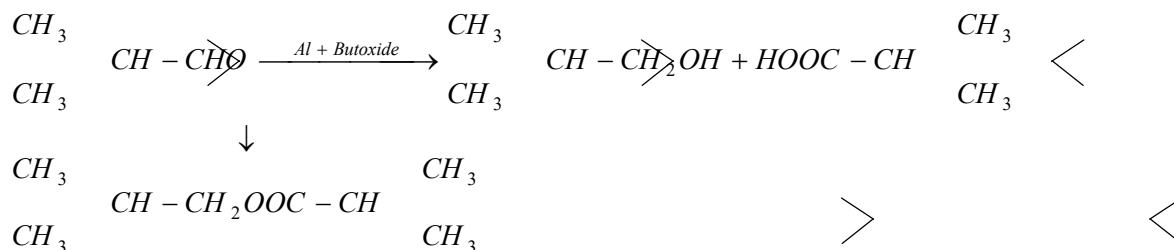
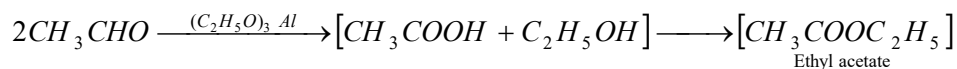
Hexamethylenetetramine has a cyclic structure. It is used as medicine in case of urinary troubles under the name of **Urotropine** or hexamine.

(ii) **Reaction with sodium hydroxide (Cannizzaro's reaction):** It does not form resin with sodium hydroxide like acetaldehyde but when treated with a concentrated solution of sodium hydroxide, two molecules of formaldehyde undergo mutual oxidation and reduction forming formic acid salt and methyl alcohol (Disproportionation).

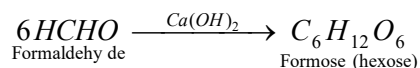


This transformation is known as Cannizzaro's reaction.

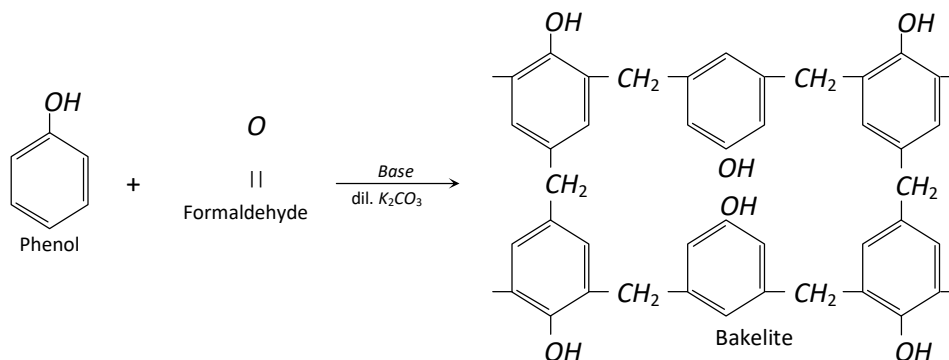
**Tischenko's reaction:** This is a modified form of Cannizzaro's reaction. All aldehydes undergo Cannizzaro's reaction in presence of aluminium ethoxide. The acid and alcohol formed react together to give the ester.



(iii) **Aldol condensation:** Formaldehyde in presence of a weak base undergo repeated aldol condensation to give formose ( $\alpha$ -acrose).

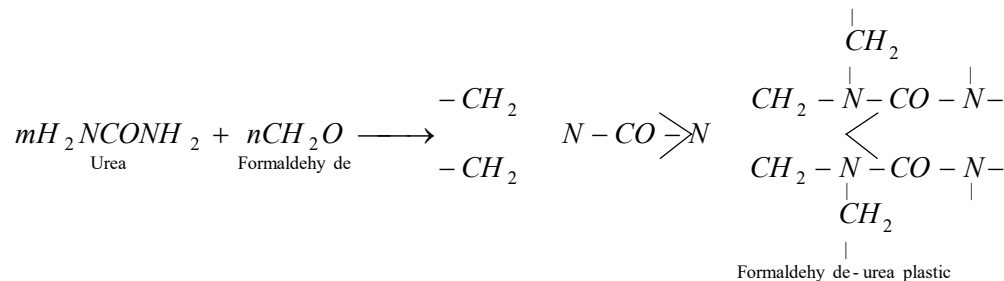


(iv) **Condensation with phenol:** Formaldehyde condenses with phenol to give a synthetic plastic, bakelite. The condensation occurs in presence of dilute sodium hydroxide or ammonia at 80 – 90°C. Bakelite is used for preparing electrical insulators, electric switches, toys, etc.

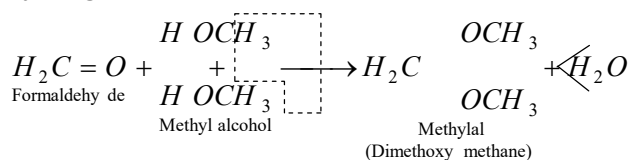


Bakelite is electrical and thermal resistant so it is used in formation of electrical appliances. This reaction is called Lederer- Manasse reaction.

(v) **Condensation with urea:** Formaldehyde also condenses with urea in acidic solution to form a plastic like product.

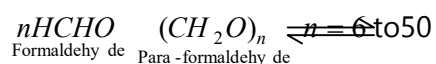


(vi) **Reaction with alcohol:** Formaldehyde reacts with methyl alcohol in presence of dry hydrogen chloride or fused calcium chloride forming methylal which is used as soporific.



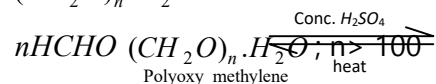
(vii) **Polymerisation:** Formaldehyde readily undergoes polymerisation.

(a) Paraformaldehyde: When an aqueous solution of formaldehyde is evaporated to dryness, a white crystalline solid with fishy odour is obtained. It is a long chain polymer.



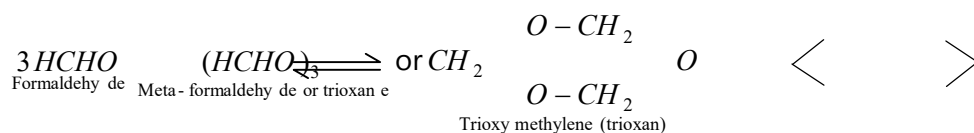
On rapid heating it gives back gaseous formaldehyde.

When a formaldehyde solution is treated with con.  $H_2SO_4$ , a white solid, polyoxymethylenes  $(CH_2O)_n \cdot H_2O$  are formed.

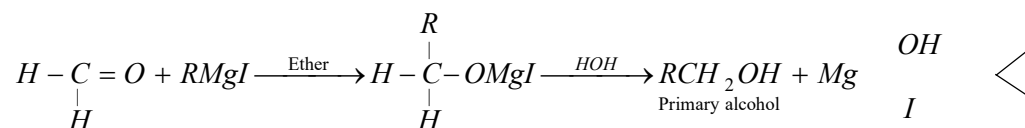


This on heating gives back formaldehyde.

(b) Metaformaldehyde: On allowing formaldehyde gas to stand at room temperature, it slowly polymerises to metaform,  $(HCHO)_3$ . It is a white solid (m.pt. 61 – 62°C). This on heating gives back gaseous formaldehyde.



(viii) **Reaction with grignard reagent:** Formaldehyde forms primary alcohols with Grignard reagent.



Formaldehyde does not react with chlorine and phosphorus pentachloride. It does not give iodoform test.

#### (4) Uses

(i) The 40% solution of formaldehyde (formalin) is used as disinfectant, germicide and antiseptic. It is used for the preservation of biological specimens.

(ii) It is used in the preparation of hexamethylenetetramine (urotropine) which is used as an antiseptic and germicide.

(iii) It is used in silvering of mirror.

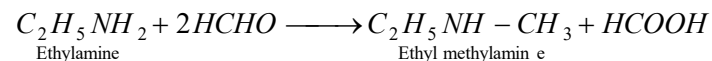
(iv) It is employed in manufacture of synthetic dyes such as para-rosaniline, indigo, etc.

(v) It is used in the manufacture of **formamint**(by mixing formaldehyde with lactose) – a throat lozenges.

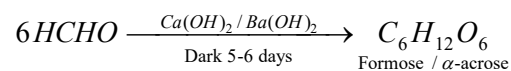
(vi) It is used for making synthetic plastics like bakelite, urea-formaldehyde resin, etc.

(vii) Rongalite – a product obtained by reducing formaldehyde sodium bisulphite derivative with zinc dust and ammonia and is used as a reducing agent in vat dyeing.

(viii) As a methylating agent for primary and secondary amines, e.g.,



(ix) If aqueous solution of formaldehyde is kept with lime water in dark room for 5 – 6 days then it converts into a sweet solution called formose or  $\alpha$ -acrose. It is an example of linear polymer.



#### Acetaldehyde

Acetaldehyde is the second member of the aldehyde series. It occurs in certain fruits. It was first prepared by Scheele in 1774 by oxidation of ethyl alcohol.

(1) **Preparation:** It may be prepared by any of the general methods. The summary of the methods is given below

(i) By oxidation of ethyl alcohol with acidified potassium dichromate or with air in presence of a catalyst like silver at 300°C.

(ii) By dehydrogenation of ethyl alcohol. The vapours of ethyl alcohol are passed over copper at 300°C.

(iii) By heating the mixture of calcium acetate and calcium formate.

(iv) By heating ethylidene chloride with caustic soda or caustic potash solution.

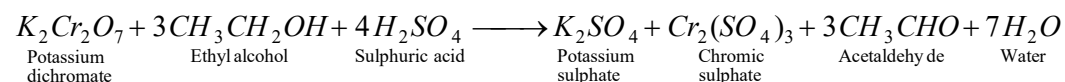
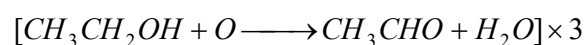
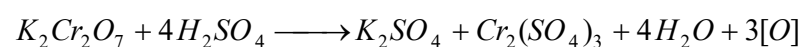
(v) By the reduction of acetyl chloride with hydrogen in presence of a catalyst palladium suspended in barium sulphate (Rosenmund's reaction).

(vi) By the reduction of  $CH_3CN$  with stannous chloride and HCl in ether and hydrolysis (Stephen's method).

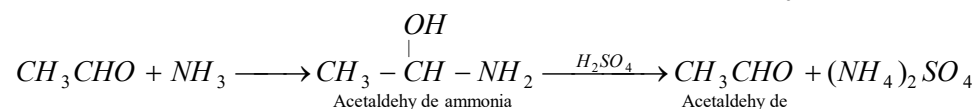
(vii) By hydration of acetylene with dil.  $H_2SO_4$  and  $HgSO_4$  at  $60^\circ C$ .

(viii) By ozonolysis of butene-2 and subsequent breaking of ozonide.

(ix) **Laboratory preparation:** Acetaldehyde is prepared in the laboratory by oxidation of ethyl alcohol with acidified potassium dichromate or acidified sodium dichromate.

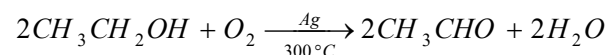


To recover acetaldehyde, the distillate is treated with dry ammonia when crystallised product, acetaldehyde ammonia, is formed. It is filtered and washed with dry ether. The dried crystals are then distilled with dilute sulphuric acid when pure acetaldehyde is collected.

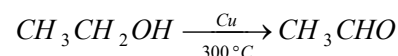


(x) **Manufacture :** Acetaldehyde can be manufactured by one of the following methods:

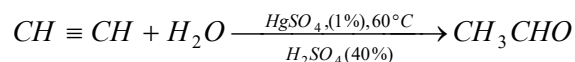
(a) By air oxidation of ethyl alcohol: Ethyl alcohol vapours and limited amount of air are passed over heated silver catalyst at  $300^\circ C$ .



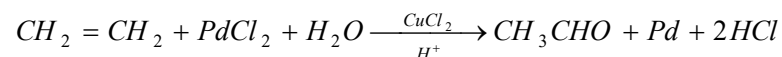
(b) By dehydrogenation of alcohol: Vapours of ethyl alcohol are passed over heated copper at  $300^\circ C$ .

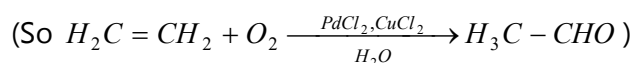
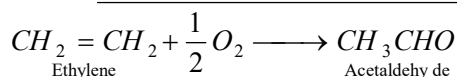
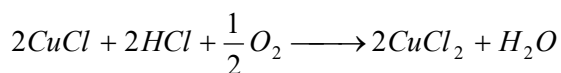
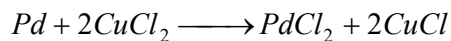


(c) By hydration of acetylene : Acetylene is passed through water containing 40% sulphuric acid and 1% mercuric sulphate at  $60^\circ C$  when acetaldehyde is formed.



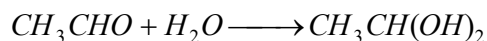
(d) From ethylene (Wacker process): Ethylene is passed through an acidified aqueous solution of palladium chloride and cupric chloride, when acetaldehyde is formed.





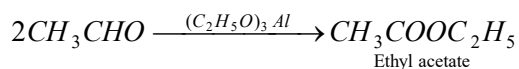
## (2) Physical properties

- (i) Acetaldehyde is a colourless volatile liquid. It boils at 21°C.
- (ii) It has a characteristic pungent smell.
- (iii) It is soluble in water, chloroform, ethyl alcohol and ether. Its aqueous solution has a pleasant odour. In water, it is hydrated to a considerable extent to form ethylidene glycol.

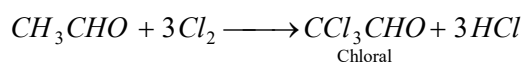


(3) **Chemical properties:** It gives all characteristic reactions of aldehydes. Besides general reactions, acetaldehyde shows the following reactions also.

- (i) **Haloform reaction:** It responds to iodoform reaction due to the presence of  $CH_3CO$  group.
- (ii) **Tischenko's reaction:** It forms ethyl acetate in presence of aluminium ethoxide.

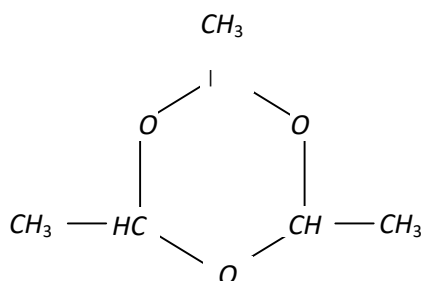
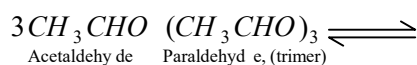


(iii) **Chlorination:** Hydrogen atoms of the methyl group are substituted by chlorine atoms when acetaldehyde is treated with chlorine.

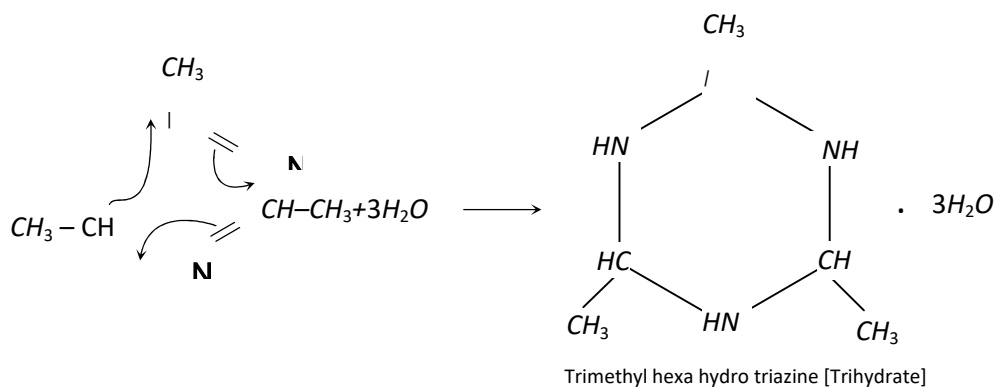
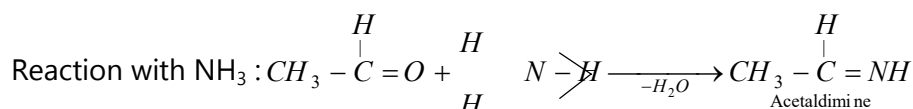


(iv) **Polymerisation:** Acetaldehyde undergoes polymerisation forming different products under different conditions.

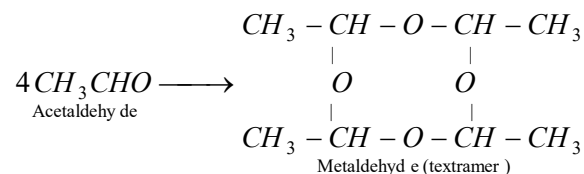
(a) Paraldehyde: It is formed, when anhydrous acetaldehyde is treated with conc. sulphuric acid.



It is a pleasant smelling liquid (b.pt. 124°C). It has cyclic structure and when heated with dilute sulphuric acid it changes again into acetaldehyde. It is used as a hypnotic and soporific (sleep producing).



(b) Metaldehyde: Acetaldehyde on treatment with hydrogen chloride or sulphur dioxide is converted into metaldehyde  $(\text{CH}_3\text{CHO})_4$ . It is a white solid (m. pt. 246°C). On heating it sublimes but changes again into acetaldehyde when distilled with dilute sulphuric acid. It is used as a solid fuel.



It is used for killing slugs and snails.



(4) **Uses:** Acetaldehyde is used :

(i) In the preparation of acetic acid, acetic anhydride, ethyl acetate, chloral, 1,3-butadiene (used in rubbers), dyes and drugs.

(ii) As an antiseptic inhalant in nose troubles.

(iii) In the preparation of paraldehyde (hypnotic and sporofic) and metaldehyde (solid fuel).

(iv) In the preparation of acetaldehyde ammonia (a rubber accelerator).

### Comparative study of formaldehyde and acetaldehyde

S.No	Reaction	Formaldehyde HCHO	Acetaldehyde CH <sub>3</sub> CHO
1.	<b>Similarity</b> Addition of hydrogen (a) H <sub>2</sub> in presence of catalyst, Ni, Pd or Pt (b) LiAlH <sub>4</sub> (ether) (c) Amalgamated zinc + conc. HCl (Clemmensen reduction)	Forms methyl alcohol $HCHO + H_2 \longrightarrow CH_3OH$ Forms methane $HCHO + 4H \longrightarrow CH_4 + H_2O$	Forms ethyl alcohol $CH_3CHO + H_2 \longrightarrow CH_3CH_2OH$ Forms ethyl alcohol Forms ethane $CH_3CHO + 4H \longrightarrow C_2H_6 + H_2O$
2.	Addition of NaHSO <sub>3</sub> solution	Forms bisulphite addition product $HCHO + NaHSO_3 \longrightarrow CH_2(OH)SO_3Na$	Forms bisulphite addition product $CH_3CHO + NaHSO_3 \longrightarrow$ $CH_3CH(OH)SO_3Na$
3.	Addition of HCN	Forms formaldehyde cyanohydrin $HCHO + HCN \longrightarrow CH_2(OH)CN$	Forms acetaldehyde cyanohydrin $CH_3CHO + HCN \longrightarrow$ $CH_3CH(OH)CN$
4.	Addition of Grignard reagent followed by hydrolysis	Forms ethyl alcohol $<$	Forms isopropyl alcohol $CH_3CHO + CH_3MgI \longrightarrow$

		$HCHO + CH_3MgI \xrightarrow{OMgI} \begin{matrix} CH_2 \\   \\ CH_3 \end{matrix}$ $\xrightarrow[-Mg(OH)I]{H_2O} CH_3CH_2OH$	$CH_3 - C \begin{matrix} HOMgI \\   \\ CH_3 \end{matrix} \xrightarrow[-Mg(OH)I]{H_2O}$ $CH_3 - \begin{matrix} CH - OH \\   \\ CH_3 \end{matrix}$
5.	With hydroxylamine $NH_2OH$	Forms formaldoxime $CH_2 = O + H_2NOH \xrightarrow{-H_2O}$ $CH_2 = NOH$	Forms acetaldoxime $CH_3CH = O + H_2NOH \xrightarrow{-H_2O}$ $CH_3CH = NOH$
6.	With hydrazine $(NH_2NH_2)$	Forms formaldehyde hydrazone $CH_2O + H_2NNH_2 \xrightarrow{-H_2O}$ $CH_2 = NNH_2$	Forms acetaldehyde hydrazone $CH_3CH = O + H_2NNH_2 \xrightarrow{-H_2O}$ $CH_3CH = NNH_2$
7.	With phenyl hydrazine $(C_6H_5NHNH_2)$	Forms formaldehyde phenyl hydrazone $CH_2 = O + H_2NNHC_6H_5 \xrightarrow{-H_2O}$ $CH_2 = NNHC_6H_5$	Forms acetaldehyde phenyl hydrazone $CH_3CH = O + H_2NNHC_6H_5 \xrightarrow{-H_2O}$ $CH_3CH = NNHC_6H_5$
8.	With semicarbazide $(H_2NNHCONH_2)$	Forms formaldehyde semicarbazone $CH_2 = O + H_2NNHCONH_2 \xrightarrow{-H_2O}$ $CH_2 = NNHCONH_2$	Forms acetaldehyde semicarbazone $CH_3CH = O + H_2NNHCONH_2 \xrightarrow{-H_2O}$ $CH_3CH = NNHCONH_2$
9.	With alcohol $(C_2H_5OH)$ in presence of acid	Forms ethylal $H_2C = O + 2C_2H_5OH \xrightarrow{HCl}$ $CH_2 \begin{matrix} OC_2H_5 \\   \\ OC_2H_5 \end{matrix} <$	Forms acetaldehyde diethyl acetal $CH_3CHO + 2C_2H_5OH \xrightarrow{HCl}$ $CH_3CH \begin{matrix} OC_2H_5 \\   \\ OC_2H_5 \end{matrix} <$
10.	With thioalcohols $(C_2H_5SH)$ in presence of acid	Forms thio ethylal $H_2C = O + 2C_2H_5SH \xrightarrow{HCl}$ $CH_2 \begin{matrix} SC_2H_5 \\   \\ SC_2H_5 \end{matrix} <$	Forms acetaldehyde diethyl thioacetal $CH_3CH = O + 2C_2H_5SH \xrightarrow{HCl}$ $CH_3CH \begin{matrix} SC_2H_5 \\   \\ SC_2H_5 \end{matrix} <$
11.	Oxidation with acidified $K_2Cr_2O_7$	Forms formic acid	Forms acetic acid

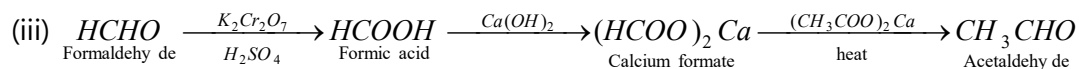
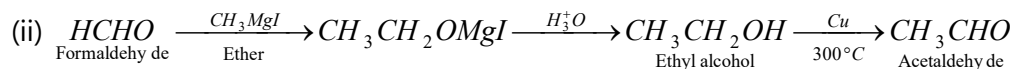
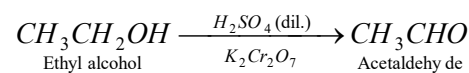
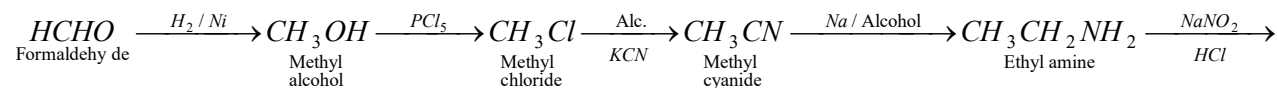
		$HCHO + O \longrightarrow HCOOH$	$CH_3CHO + O \longrightarrow CH_3COOH$
12.	With Schiff's reagent	Restores pink colour of Schiff's reagent	Restores pink colour of Schiff's reagent
13.	With Tollen's reagent	Gives black precipitate of Ag or silver mirror $Ag_2O + HCHO \longrightarrow 2Ag + HCOOH$	Gives black precipitate of Ag or silver mirror $Ag_2O + CH_3CHO \longrightarrow 2Ag + CH_3COOH$
14.	With Fehling's solution or Benedict's solution	Gives red precipitate of cuprous oxide $2CuO + HCHO \longrightarrow Cu_2O + HCOOH$	Gives red precipitate of cuprous oxide $2CuO + CH_3CHO \longrightarrow Cu_2O + CH_3COOH$
15.	Polymerisation	Undergoes polymerisation $nHCHO \xrightarrow[\text{Room temp.}]{\text{Evaporation}} (HCHO)_n$ Paraformaldehyde $3HCHO \xrightarrow[\text{Heat}]{\text{Heat}} (HCHO)_3$ Metaformaldehyde	Undergoes polymerisation $3CH_3CHO \xrightarrow[\text{dil. } H_2SO_4, \text{ distill.}]{H_2SO_4, \text{ Conc.}} (CH_3CHO)_3$ Paraldehyde $4CH_3CHO \xrightarrow{\text{Heat}} (CH_3CHO)_4$ Metaldehyde
16.	<b>Difference</b> With $PCl_5$	No reaction	Forms ethylidene chloride $CH_3CHO + PCl_5 \longrightarrow CH_3CH \begin{matrix} \diagdown \\ Cl \\ \diagup \\ Cl \end{matrix} + POCl_3$
17.	With chlorine	No reaction	Forms chloral $CH_3CHO + 3Cl_2 \longrightarrow CCl_3CHO + 3HCl$
18.	With $SeO_2$	No reaction	Forms glyoxal $CH_3CHO + SeO_2 \longrightarrow CHO \cdot CHO + Se + H_2O$
19.	Iodoform reaction ( $I_2 + NaOH$ )	No reaction	Forms iodoform $CH_3CHO + 3I_2 + 4NaOH \longrightarrow CHI_3 + HCOONa + 3NaI + 3H_2O$
20.	With dil. alkali (Aldol condensation)	No reaction	Forms aldol $CH_3CHO + HCHO \longrightarrow CH_3CH(OH)CH_2CHO$
21.	With conc. NaOH (Cannizzaro's)	Forms sodium formate and	Forms a brown resinous mass

	reaction)	methyl alcohol $2HCHO + NaOH \longrightarrow HCOONa$ $+CH_3OH$	
22.	With ammonia	Forms hexamethylenetetramine (urotropine) $6HCHO + 4NH_3 \longrightarrow (CH_2)_6N_4 + 6H_2O$	Forms addition product, acetaldehyde ammonia $CH_3CHO + NH_3 \longrightarrow$ $\begin{matrix} OH \\ CH_3CH \\ NH_2 \end{matrix}$
23.	With phenol	Forms bakelite plastic	No reaction
24.	With urea	Forms urea-formaldehyde plastic	No reaction
25.	Condensation in presence of $Ca(OH)_2$	Form formose (a mixture of sugars)	No reaction

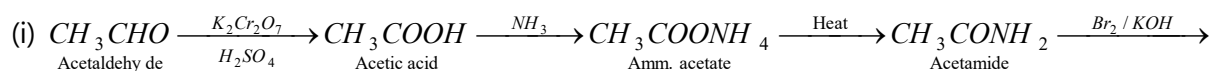
### Inter conversion of formaldehyde and acetaldehyde

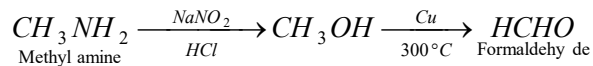
(1) **Ascent of series:** Conversion of formaldehyde into acetaldehyde

(i)

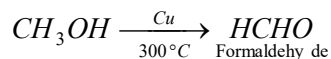


(2) **Descent of series:** Conversion of acetaldehyde into formaldehyde





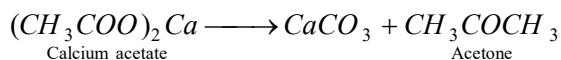
(ii)



## Acetone

It is a symmetrical (simple) ketone and is the first member of the homologous series of ketones. In traces, it is present in blood and urine.

(1) **Laboratory preparation:** Acetone is prepared in laboratory by heating anhydrous calcium acetate.



The retort is heated slowly when acetone distills over and collected in the receiver.

The distillate is shaken with saturated solution of sodium bisulphite when colourless crystals are formed. These are filtered and distilled with saturated solution of sodium carbonate. The aqueous solution of acetone is dried over anhydrous calcium chloride and redistilled to obtain pure acetone. The fraction is collected between 55 to 57° C (b.pt. pure acetone 56° C).

