Tri-halides (Chloroform and iodoform).

Chloroform or trichloromethane, $CHCl_3$

It is an important trihalogen derivative of methane. It was discovered by Liebig in 1831 and its name chloroform was proposed by Dumas as it gave formic acid on hydrolysis. In the past, it was extensively used as anaesthetic for surgery but now it is rarely used as it causes liver damage.

(1) Preparation

(i) Chloroform is prepared both in the laboratory and on large scale by distilling ethyl alcohol or acetone with bleaching powder and water. The yield is about 40%. The available chlorine of bleaching powder serves both as oxidising as well as chlorinating agent.

$$\underset{\text{Bleaching powder}}{CaOCl_2} + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

(a) From alcohol

❑ Alcohol is first oxidised to acetaldehyde by chlorine.

$$[Cl_2 + H_2O \longrightarrow 2HCl + O]; \quad \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + O \longrightarrow \underset{\text{Acetaldehy de}}{CH_3CHO} + H_2O$$

❑ Acetaldehyde then reacts with chlorine to form chloral (Trichloro acetaldehyde).

$$\underset{\text{Acetaldehy de}}{CH_3CHO} + 3Cl_2 \longrightarrow \underset{\text{Chloral}}{CCl_3CHO} + 3HCl$$

[So Cl_2 acts both as an oxidising and chlorinating agent]

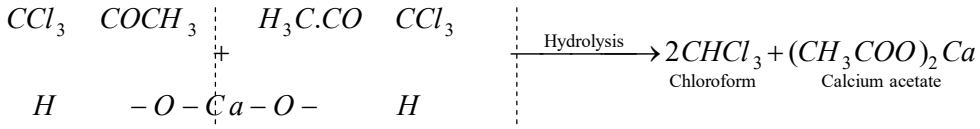
Chloral, thus, formed, is hydrolysed by calcium hydroxide.

$$\begin{array}{l} CCl_3\ CHO \qquad OHC\ CCl_3 \\ \qquad\qquad + \\ H\quad -O-Ca-O-\quad H \end{array} \xrightarrow{\text{Hydrolysis}} \underset{\text{Chloroform}}{2CHCl_3} + \underset{\text{Calcium formate}}{(HCOO)_2Ca}$$

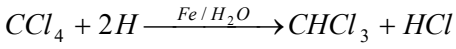
(b) From acetone: Acetone first reacts with chlorine to form trichloro acetone.

$$CH_3 - CO - CH_3 + 3Cl_2 \longrightarrow \underset{\text{Trichloro acetone}}{CCl_3COCH_3} + 3HCl$$

❑Trichloro acetone is then hydrolysed by calcium hydroxide.

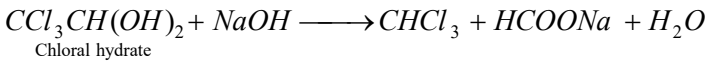


(ii) From carbon tetrachloride: Now-a-days, chloroform is obtained on a large scale by the reduction of carbon tetrachloride with iron fillings and water. This method is used in countries like U.S.A.

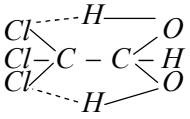


This chloroform is not pure and used mainly as a solvent.

(iii) Pure Chloroform is obtained by distilling chloral hydrate with concentrated sodium hydroxide solution.



Note: Chloral hydrate is a stable compound inspite of the fact that two $-OH$ groups are linked to the same carbon atom. This is due to the fact that intramolecular hydrogen bonding exists in the molecule between chlorine and hydrogen atom of $-OH$ group.



(2) Physical properties

(i) It is a sweet smelling colorless liquid.

(ii) It is heavy liquid. Its density is 1.485. It boils at 61°C.

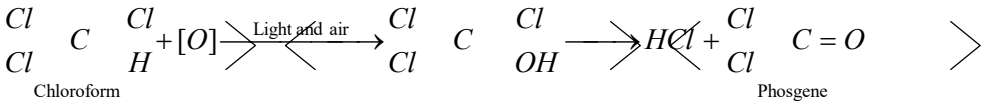
(iii) It is practically insoluble in water but dissolves in organic solvents such as alcohol, ether, etc.

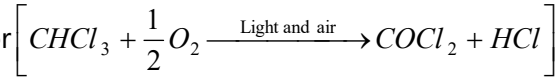
(iv) It is non-inflammable but its vapours may burn with green flame.

(v) It brings temporary unconsciousness when vapours are inhaled for sufficient time.

(3) Chemical properties

(i) Oxidation: When exposed to sunlight and air, it slowly decomposes into phosgene and hydrogen chloride.



or 

Phosgene is extremely poisonous gas. To use chloroform as an anaesthetic agent, it is necessary to prevent the above reaction. The following two precautions are taken when chloroform is stored.

(a) It is stored in dark blue or brown coloured bottles, which are filled upto the brim.

(b) 1% ethyl alcohol is added. This retards the oxidation and converts the phosgene formed into harmless ethyl carbonate.

$$COCl_2 + 2C_2H_5OH \longrightarrow \underset{\text{Ethyl carbonate}}{(C_2H_5O)_2CO} + 2HCl$$

(ii) Reduction: When reduced with zinc and hydrochloric acid in presence of ethyl alcohol, it forms methylene chloride.

$$CHCl_3 + 2H \xrightarrow[\text{(alc.)}]{Zn/HCl} CH_2Cl_2 + HCl$$

When reduced with zinc dust and water, methane is the main product.

$$CHCl_3 + 6H \xrightarrow{Zn/H_2O} CH_4 + 3HCl$$

(iii) Chlorination: Chloroform reacts with chlorine in presence of diffused sunlight or UV light to form carbon tetrachloride.

$$CHCl_3 + Cl_2 \xrightarrow{\text{UV light}} \underset{\text{Carbon tetrachlo ride}}{CCl_4} + HCl$$

(iv) Hydrolysis: Chloroform is hydrolysed when treated with hot aqueous solution of sodium hydroxide or potassium hydroxide. The final product is sodium or potassium salt of formic acid.

$$H-C \begin{matrix} Cl+Na\ OH(aq.) \\ Cl+Na\ OH(aq.) \\ Cl+Na\ OH(aq.) \end{matrix} \xrightarrow{-NaCl} \underset{\substack{\text{Unstable} \\ \text{(Orthoform ic acid)}}}{\begin{bmatrix} HC & OH \\ & OH \\ & OH \end{bmatrix}} \xrightarrow{-H_2O} \underset{\text{Formic acid}}{H-C \begin{matrix} O \\ OH \end{matrix}} \xrightarrow[-H_2O]{NaOH} \underset{\text{Sodium formate}}{H-C \begin{matrix} O \\ ONa \end{matrix}}$$

[So, $CHCl_3 + 4KOH(aq.) \xrightarrow{\text{Hydrolysis}} HCOOK + 3KCl + 2H_2O$]

(v) Nitration: The hydrogen of the chloroform is replaced by nitro group when it is treated with concentrated nitric acid. The product formed is chloropicrin or trichloronitro methane or nitro chloroform. It is a liquid, poisonous and used as an insecticide and a war gas.

$$CHCl_3 + \underset{\text{Nitric acid}}{HONO_2} \longrightarrow \underset{\text{Chloropicr in (Tear gas)}}{CNO_2Cl_3} + H_2O$$

(vi) Heating with silver powder: Acetylene is formed when chloroform is heated at high temperature with silver powder.

$$H-C-Cl_3 + 6Ag + Cl_3-C-H \longrightarrow \underset{\text{Acetylene}}{CH \equiv CH} + 6AgCl$$

(vii) Condensation with acetone: Chloroform condenses with acetone on heating in presence of caustic alkalies. The product formed is a colourless crystalline solid called chloretone and is used as hypnotic in medicine.

$$Cl_3CH + O=C \begin{matrix} CH_3 \\ CH_3 \end{matrix} \xrightarrow{(NaOH)} \underset{\text{Chloretone}}{\underset{\text{(1,1,1 - Trichloro - 2 - methyl - 2 - propanol)}}{\begin{matrix} HO \\ Cl_3C \end{matrix} C \begin{matrix} CH_3 \\ CH_3 \end{matrix}}}$$

(viii) Reaction with sodium ethoxide: When heated with sodium ethoxide, ethyl orthoformate is formed.

$$H-C \begin{matrix} Cl + Na\ OC_2H_5 \\ Cl + Na\ OC_2H_5 \\ Cl + Na\ OC_2H_5 \end{matrix} \xrightarrow{-3\,NaCl} H-C \begin{matrix} OC_2H_5 \\ OC_2H_5 \\ OC_2H_5 \end{matrix}$$

Ethyl orthoforma te

(ix) **Reimer-Tiemann reaction**: Chloroform reacts with phenol when heated in presence of sodium hydroxide or potassium hydroxide. The product formed is salicylaldehyde.

$$C_6H_5OH + CHCl_3 + 3NaOH \xrightarrow{65^\circ C} C_6H_4 \begin{matrix} OH \\ CHO \end{matrix} + 3NaCl + 2H_2O$$

Hydroxy benzaldeh yde

(x) **Carbylamine reaction** (Isocyanide test): This reaction is actually the test of primary amines. Chloroform, when heated with primary amine in presence of alcoholic potassium hydroxide forms a derivative called isocyanide which has a very offensive smell.

$$RNH_2 + CHCl_3 + 3KOH(alc.) \xrightarrow{\Delta} \underset{\substack{\text{Carbylamin oalkane} \\ \text{(Alkylisonitrile)}}}{RNC} + 3KCl + 3H_2O$$

This reaction is also used for the test of chloroform.

(4) **Uses**

(i) It is used as a solvent for fats, waxes, rubber, resins, iodine, etc.

(ii) It is used for the preparation of chloretone (a drug) and chloropicrin (Insecticide).

(iii) It is used in laboratory for the test of primary amines, iodides and bromides.

(iv) It can be used as **anaesthetic**but due to harmful effects it is not used these days for this purpose.

(v) It may be used to prevent putrefaction of organic materials, i.e., in the preservation of anatomical species.

(5) **Tests of chloroform**

(i) It gives isocyanide test (Carbylamine test).

(ii) It forms silver mirror with Tollen's reagent.

(iii) Pure Chloroform does not give white precipitate with silver nitrate.

Iodoform or tri-iodomethane, CHI_3

Iodoform resembles chloroform in the methods of preparation and properties.

(1) **Preparation**

(i) **Laboratory preparation**: Iodoform is prepared in the laboratory by heating ethanol or acetone with iodine and alkali.

Ethanol: $CH_3CH_2OH + I_2 \longrightarrow \underset{\text{Acetaldehy de}}{CH_3CHO} + 2HI$

$CH_3CHO + 3I_2 \longrightarrow \underset{Iodal}{CI_3CHO} + 3HI$

$\underset{Tri-iodoacetaldehyde}{CI_3CHO} + KOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Pot. formate}}{HCOOK}$

Acetone**:** $CH_3COCH_3 + 3I_2 \longrightarrow \underset{\text{Tri-iodoaceton e}}{CI_3COCH_3} + 3HI$

$CI_3COCH_3 + KOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Pot. acetate}}{CH_3COOK}$

Sodium carbonate can be used in place of KOH or NaOH. These reactions are called iodoform reactions.

(ii) **Industrial preparation**: Iodoform is prepared on large scale by electrolysis of a solution containing ethanol, sodium carbonate and potassium iodide. The iodine set free, combine with ethanol in presence of alkali to form iodoform. The electrolysis carried out in presence of CO_2 and the temperature is maintained at 60-70°C.

$KI \rightleftharpoons K^+ + I^-$

Cathode ↙ ↘ Anode

$K^+ + e^- \rightarrow K \quad 2I^- \rightarrow I_2 + 2e^-$

$K + H_2O \longrightarrow KOH + \frac{1}{2}H_2$

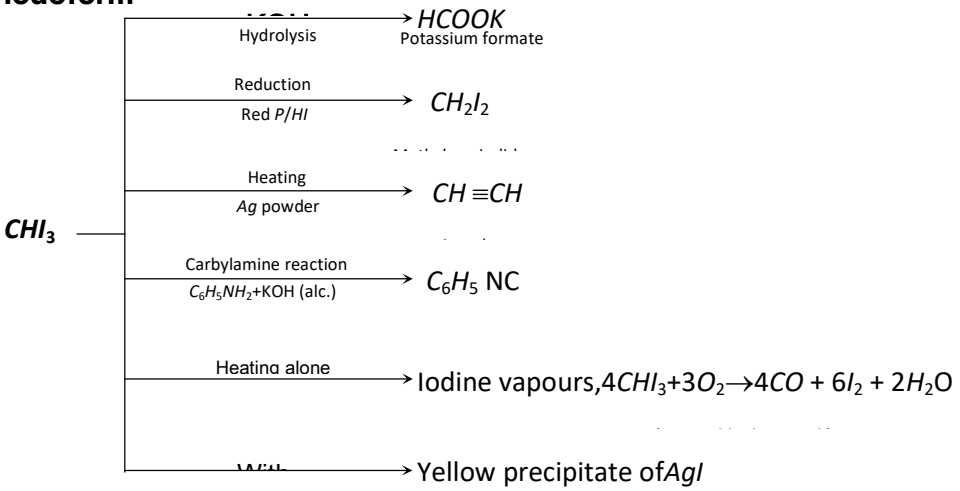
KOH is neutralisedby CO_2:

$C_2H_5OH + 4I_2 + 3Na_2CO_3 \longrightarrow CHI_3 + HCOONa + 5NaI + 3CO_2 + 2H_2O$

(2) **Properties**

(i) It is a yellow crystalline solid.
(ii) It has a pungent characteristic odour.
(iii) It is insoluble in water but soluble in organic solvents such as alcohol, ether, etc.
(iv) It has melting point 119°C. It is steam volatile.

(3) **Reactions of iodoform**



(4) **Uses:**Iodoform is extensively used as an **antiseptic** for dressing of wounds; but the antiseptic action is due to the liberation of free iodine and not due to iodoform itself. When it comes in contact with organic matter, iodine is liberated which is responsible for antiseptic properties.

(5) **Tests of iodoform**

(i) **With $AgNO_3$** : CHI_3 gives a yellow precipitate of AgI.

(ii) **Carbylamine reaction**: CHI_3 on heating with primary amine and alcoholic KOH solution, gives an offensive smell of isocyanide (Carbylamine).

(iii) **Iodoform reaction** : With I_2 and $NaOH$ or I_2 and Na_2CO_3, the iodoform test is mainly given by ethyl alcohol (CH_3CH_2OH), acetaldehyde $(CH_3-\overset{O}{\overset{\|}{C}}-H)$, α-methyl ketone or 2-one $(-\overset{O}{\overset{\|}{C}}-CH_3)$, secondary alcohols or 2-ol $(-CHOH\cdot CH_3)$ and secondary alkyl halide at

$C_2(-CHCICH_3)$. Also lactic acid ($CH_3-CHOH-COOH$), Pyruvic acid ($CH_3-\overset{\overset{O}{\|}}{C}-COOH$) and methyl phenyl ketone ($C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3$) give this test.