23

CARBONYL COMPOUNDS AND CARBOXYLIC ACIDS

Student Learning Outcomes

[C-12-D-59 to C-12-D-78]

Part 1: Aldehydes and Ketones (Carbonyl Compounds)

- State the reactions (reagents and conditions) by which aldehydes and ketones can be produced: a. the oxidation of primary alcohols using acidified $K_2Cr_2O_7$ or acidified $KMnO_4$ and distillation to produce aldehydes; b. the oxidation of secondary alcohols using acidified $K_2Cr_2O_7$ or acidified $KMnO_4$ and distillation to produce ketones.
- Describe the use of 2,4- dinitrophenylhydrazine (2,4-DNPH reagent) to detect the presence of carbonyl compounds.
- Deduce the nature (aldehyde or ketone) of an unknown carbonyl compound from the results of simple tests (Fehling's and Tollens' reagents; ease of oxidation).
- Deduce the presence of a CH_3CO-group in an aldehyde or ketone, CH_3COR, from its reaction with alkaline $I_{2(aq)}$ to form a yellow precipitate of tri-iodomethane and an ion, RCO^-_2.
- Describe: a. the reduction of aldehydes and ketones, using $NaBH_4$ or $LiAlH_4$ to produce alcohols; b. the reaction of aldehydes and ketones with HCN, KCN as catalyst, and heat to produce hydroxy nitriles exemplified by ethanal and propanone.
- Describe the mechanism of the nucleophilic addition reactions of hydrogen cyanide with aldehydes and ketones.

Part 2: Carboxylic Acids

- Recall the reactions by which carboxylic acids can be produced: a. oxidation of primary alcohols and aldehydes with acidified $K_2Cr_2O_7$ or acidified $KMnO_4$ and refluxing; b. hydrolysis of nitriles with dilute acid or dilute alkali followed by acidification; c. hydrolysis of esters with dilute acid or dilute alkali and heat followed by acidification.
- State the reaction which benzoic acid can be produced: reaction of alkylbenzene with hot alkaline $KMnO_4$ and then dilute acid, exemplified by methylbenzene.
- Describe the reaction of carboxylic acids with PCI_3 and heat, PCl_3 and heat, PCl_5, or $SOCl_2$ to form acylchlorides.
- Recognize that some carboxylic acids can be further oxidized: a) the oxidation of methanoic acid, HCOOH, with Fehling's reagent or Tollens' reagent or acidified $KMnO_4$ or acidified $K_2Cr_2O_7$ to carbon dioxide and water b) the oxidation of ethanedioic acid HOOCCOOH, with warm acidified $KMnO_4$ to carbon dioxide.
- Describe: a. the redox reaction with reactive metals to produce a salt and $H_2(g)$; b. the neutralization reaction with alkalis to produce a salt and $H_2O(I)$; c. the acid-base reaction with bicarbonates to produce a salt and $H_2O(l)$ and $CO_2(g)$; d. esterification with alcohols with concentrated H_2SO_4 as catalyst; e. reduction by $LiAlH_4$ to form a primary alcohol.
- Explain the relative acidities of carboxylic acids, phenols and alcohols.

- Explain the relative acidities of chlorine substituted carboxylic acids.

Part 3: Esters (Revisited and Expanded)

- Recall the reactions (reagents and conditions) by which esters can be produced: the condensation reaction between an alcohol and a carboxylic acid with concentrated H_2SO_4 as catalyst.
- Describe the hydrolysis of esters by dilute acid and by dilute alkali and heat.

Part 4: Acyl Chlorides (Acid Halides)

- Recall the reactions (reagents and conditions) by which acyl chlorides can be produced: reaction of carboxylic acids with PCl_3 and heat, PCL_5, or $SOCl_2$.
- Explain the relative ease of hydrolysis of acyl chlorides, alkyl chlorides and halogenoarenes (aryl chlorides).
- Describe the following reactions of acyl chlorides: a. hydrolysis on addition of water at room temperature to give the carboxylic acid and HCl; b. reaction with an alcohol at room temperature to produce an ester and Hcl; c. reaction with phenol at room temperature to produce and ester and HCl; d. reaction with ammonia at room temperatures to produce and amide and HCl; e. reaction with a primary or secondary amine at room temperature to produce an amide and Hcl.
- Describe the addition-elimination mechanism of acyl chlorides in reactions.
- Recall the reaction by which esters can be produced: reaction of alcohols with acyl chlorides using the formation of ethyl ethanoate and phenyl benzoate as examples.

23.1 CARBONYL COMPOUNDS

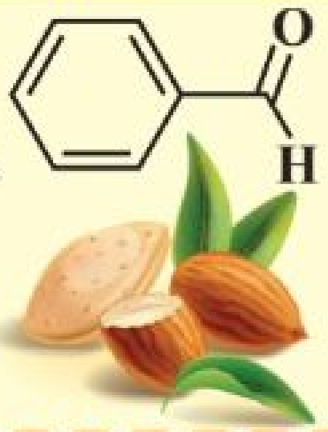
In organic chemistry, the structural unit $>CO=$ is known as carbonyl group. Aldehydes and ketones are the classes of compounds that contain a carbonyl group. The general structures of aldehydes and ketones are given below.

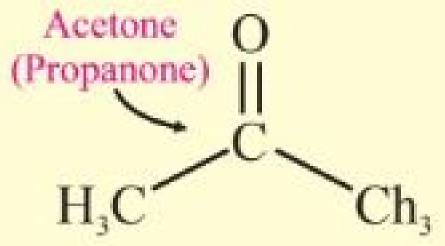
These compounds are abundant in nature and their large quantities are synthesised every year. Aldehydes are present in many spices, fruits, and natural fragrances. Ketones used in pharmaceuticals, chemicals, and paint industries. The most common ketone is acetone, which is found in nail polish removers.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H \qquad R-\overset{\overset{\displaystyle O}{\|}}{C}-R$$

Interesting Information

The smell and taste of bitter almond is due to benzaldehyde, which is produced due to the oxidation of terpenes.

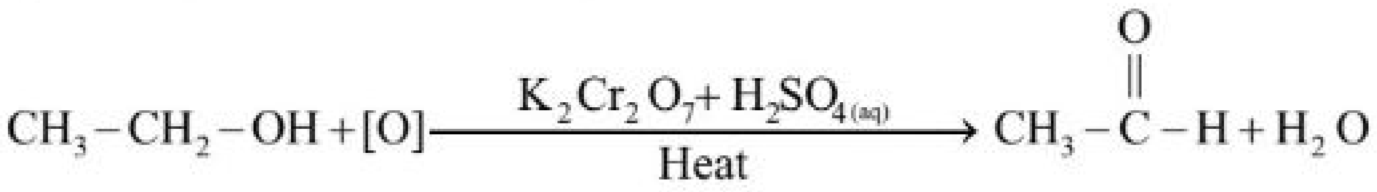




Acetone (propanone) are used in nail polish removers

23.1.1 Preparation of Aldehydes

Aldehydes are prepared by the oxidation of primary alcohols with acidified $K_2Cr_2O_7$ or acidified $KMnO_4$.



$$CH_3-CH_2-OH+[O]\xrightarrow[\text{Heat}]{K_2Cr_2O_7+H_2SO_{4(aq)}}CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H+H_2O$$

In the example of the preparation of ethanol, the acidified $K_2Cr_2O_7$ is added drop wise to the warm ethanol. The aldehyde produced is distilled off as soon as it is formed. This prevents the further oxidation of ethanal to ethanoic acids. The temperature is kept above the boiling point of acetaldehyde but below to that of ethanol, since ethanol has higher boiling point than that of acetaldehyde. Pure ethanal is obtained by redistillation. Ketones are also prepared by the same procedure from secondary alcohols but since ketones are not converted into carboxylic acids under these conditions, therefore ketone is not distilled off immediately.

Methanol, HCHO, is a gas at room temperature. It is often encountered as a 40 % aqueous solution called 'formalin', which has a fishy, unpleasant smell and is used for preserving biological specimens. Other short-chain aldehydes and ketones are liquids.

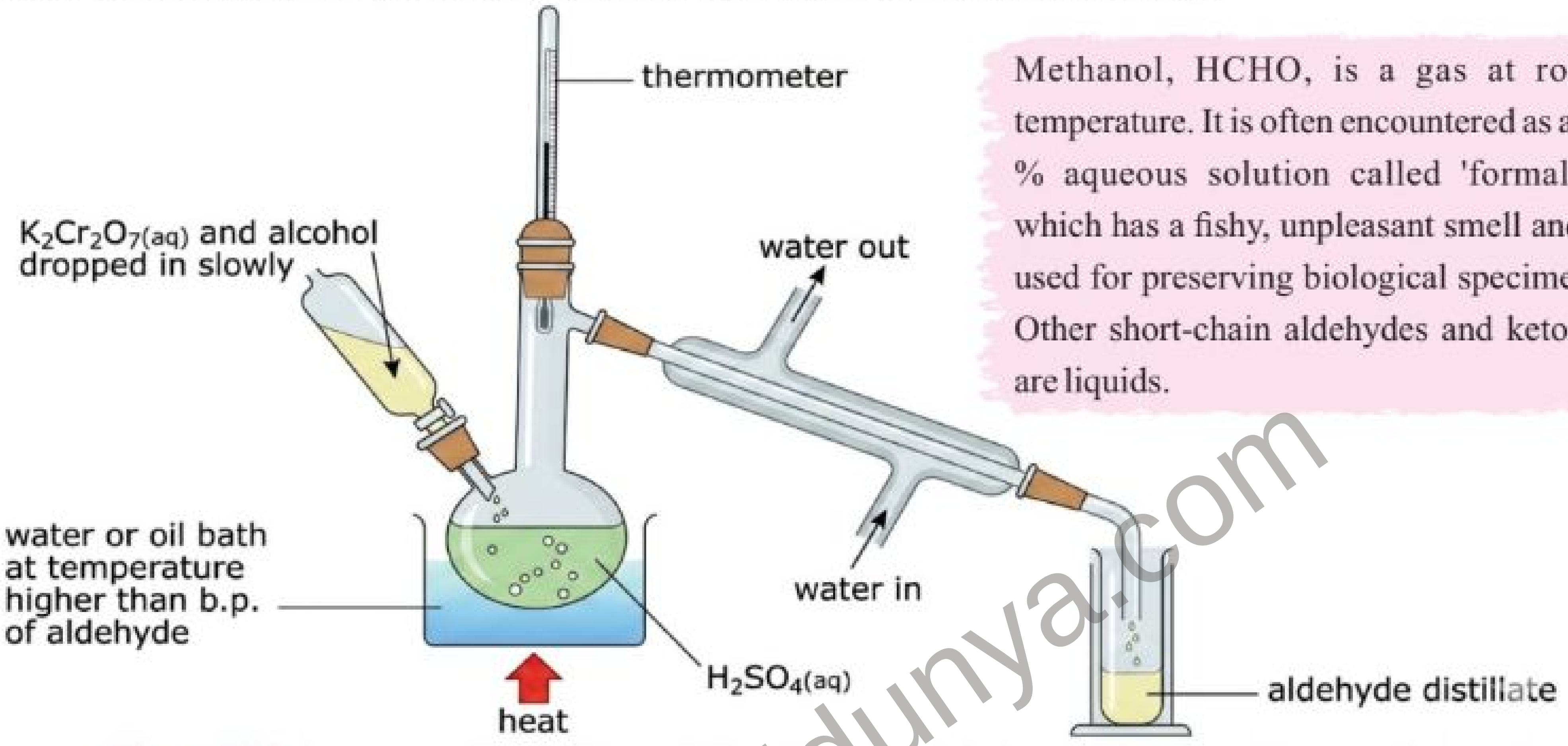
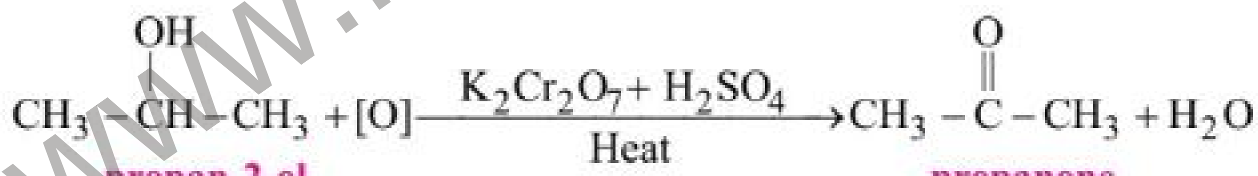


Figure 23.1 **Apparatus for distilling off the ethanal as it is formed by the oxidation of ethanol.**

23.1.2 Preparations of Ketones

Ketones are prepared by the oxidation of secondary alcohols.



$$\underset{\textbf{propan-2-ol}}{CH_3-\overset{OH}{\overset{|}{C}H}-CH_3} + [O] \xrightarrow[\text{Heat}]{K_2Cr_2O_7 + H_2SO_4} \underset{\textbf{propanone}}{CH_3-\overset{O}{\overset{||}{C}}-CH_3} + H_2O$$

23.2 CHEMISTRY OF CARBONYL COMPOUNDS

The carbonyl group , governs the chemistry of aldehydes and ketones. There are two basic reactions of carbonyl compounds.

A. Nucleophilic addition reactions
B. Alpha (α) carbon specific reactions

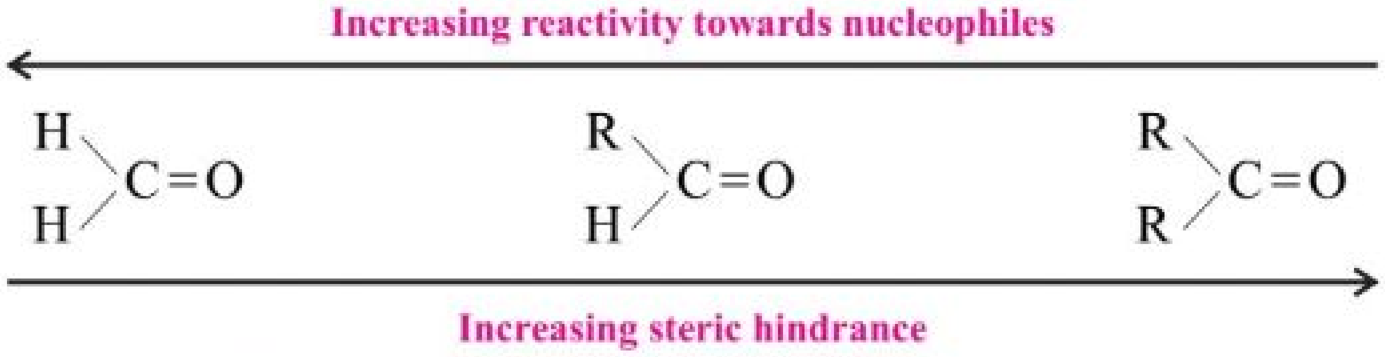
23.2.1 Structure and Reactivity of Carbonyl Group

In carbonyl group , both carbon and oxygen are sp^2 hybridized. Carbon is bonded to an oxygen atom through a double bond and to other two groups through single bonds.

Carbonyl group is polar in nature because oxygen, being more electronegative, gets partial negative charge (δ^-) and carbon gets partial positive charge (δ^+). Two structural features of the carbonyl group determine the chemistry and properties of aldehydes and ketones.

1) The carbonyl carbon is electrophilic in nature due to its δ^+ charge, and can be attacked by nucleophiles.
2) The double bond can undergo addition reactions because π bond is easily broken down. Moreover, planar shape of the group makes the carbonyl carbon uncrowded thus giving further support to addition reactions.

Aldehydes are more reactive than ketones for two reasons. First; in a ketone, the electron releasing (inductive) effect of two alkyl groups reduces the positive charge on the carbonyl carbon making it less easily attacked by nucleophiles. Secondly, the two alkyl groups of a ketone tend to get in the way of attacking nucleophiles. This is also called steric hindrance.

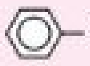


Quick Check 23.1

a) Draw the structures for the following according to IUPAC system.

i) 2-,methylbutanal ii) pentan-3-one iii) 3-methylbutenal d) 4-methylpentan-3-one

b) Name the following compounds (IUPAC) system).

i) –CHO ii) $(CH_3)_2C\text{-}CHO$ iii) $(CH_3CH_2CH_2)_2C{=}O$

c) Rank the following compounds in order of increasing reactivity towards nucleophilic attack.

i) $(CH_3)_3CCOCH_3$ ii) $(CH_3)_3CCOC(CH_3)_3$ iii) $(CH_3)_2CO$

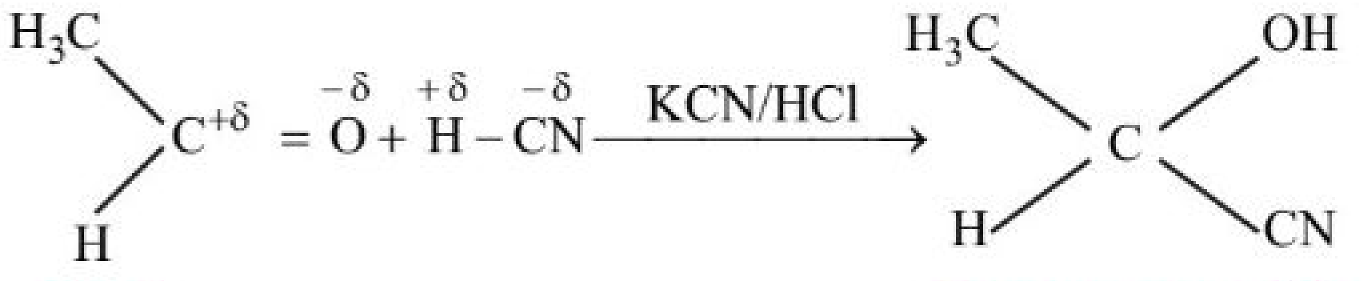
23.3 REACTIONS OF CARBONYL COMPOUNDS

23.3.1 Nucleophilic addition reactions

1. Addition of Hydrogen Cyanide (H-CN)

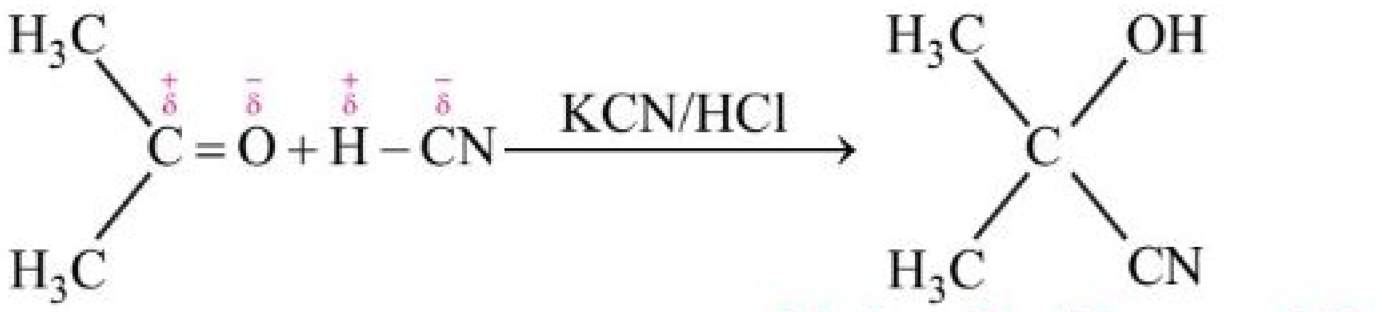
Aldehydes and ketones react with hydrogen cyanide to form cyanohydrins. HCN itself is not used directly as it is an extremely poisonous gas. Instead, it is produced by adding slowly a mineral acid (HCl) to a mixture of aqueous solution of sodium cyanide or potassium cyanide and the carbonyl compound.

2-Hydroxy-2-ethylpropanenitrile is used as an intermediate in the manufacture of Perspex, a very fine coloured-glass polymer.



ethanal

2-hydroxypropanenitrile



Mechanism

propanone

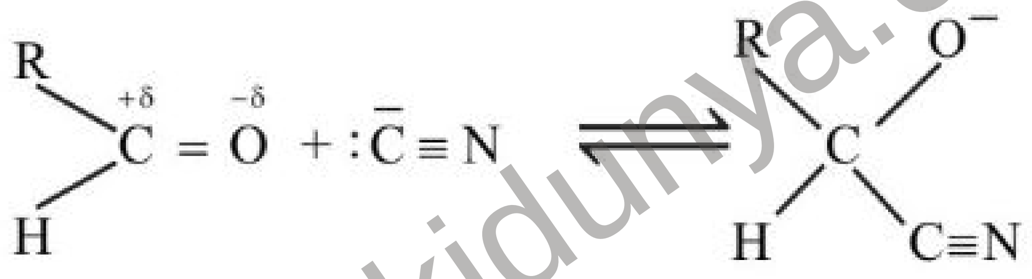
2-hydroxy-2-methlypropanenitrile

HCN is obtained by adding a controlled amount of an acid to a mixture of KCN and the carbonyl compound. The reaction between KCN and HCl produces HCN. HCN is neither a nucleophile (absence of a lone pair on the carbon atom) nor a strong acid to be ionized to a reasonable extent. Therefore it does not produce enough nucleophile (CN^-) to start a reaction and complete the reaction in a shorter time. This is done by adding a slight excess of KCN, so that there are some free CN^- ions in the solution. These free ions start the reaction and catalyse it to move at a reasonable rate.

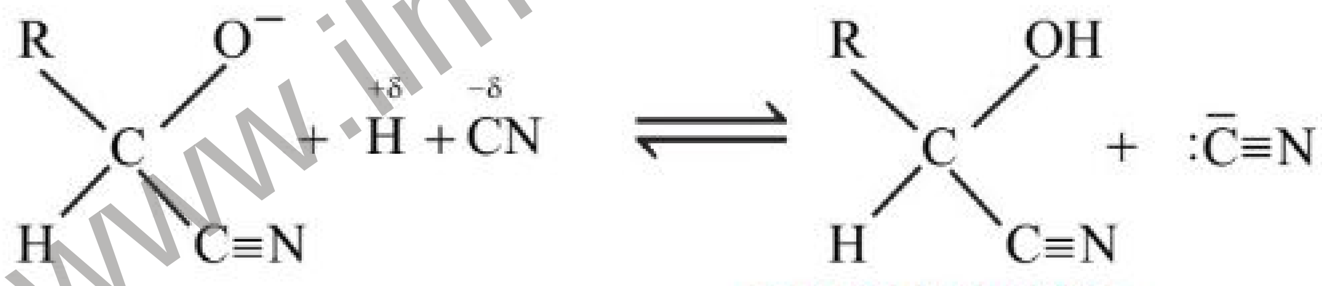
Hence,

I) $$\underset{\text{(Excess)}}{KCN} + \underset{\text{(Limiting)}}{HCl} \longrightarrow \underset{\text{(Nucleophilic Reagent)}}{HCN} + KCl$$

ii)



iii)



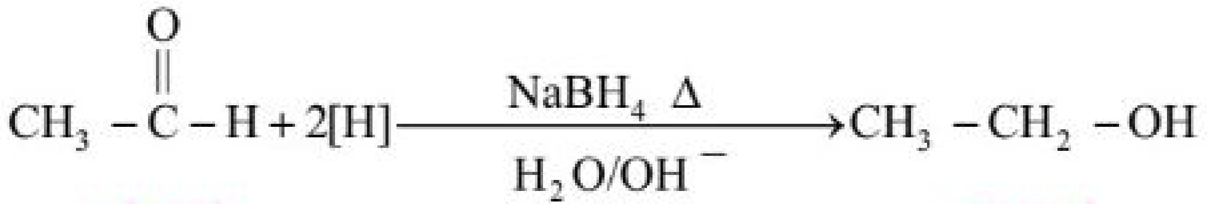
hydroxyalkanenitrile

Although both the steps involved in cyanohydrin formation are reversible, the equilibria lie far to the right. Most of carbonyl compounds giving high yields of cyanohydrins at the equilibrium. Nitriles are hydrolysed by dilute acid or aqueous alkali to form carboxylic acids or carboxylate ions; this will be discussed later.

2. Addition of hydride ion (H-)

Since aldehydes and ketones are synthesised by oxidation of alcohols, alcohols can be produced by the reduction of aldehydes and ketones. With a reducing agent such as $NaBH_4$ or $LiAlH_4$, aldehydes give primary alcohols and ketones gives secondary alcohols.

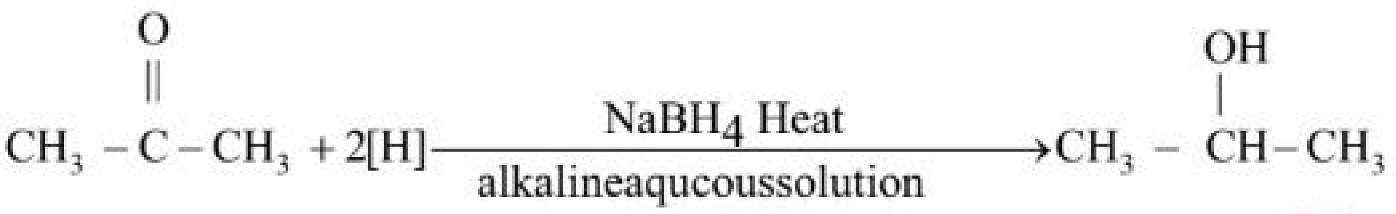
Notice that reducing H in brackets [ ] comes from $NaBH_4$ to balance the equation. It does not represent atomic hydrogen.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + 2[H] \xrightarrow[H_2O/OH^-]{NaBH_4\ \Delta} CH_3-CH_2-OH$$

ethanal

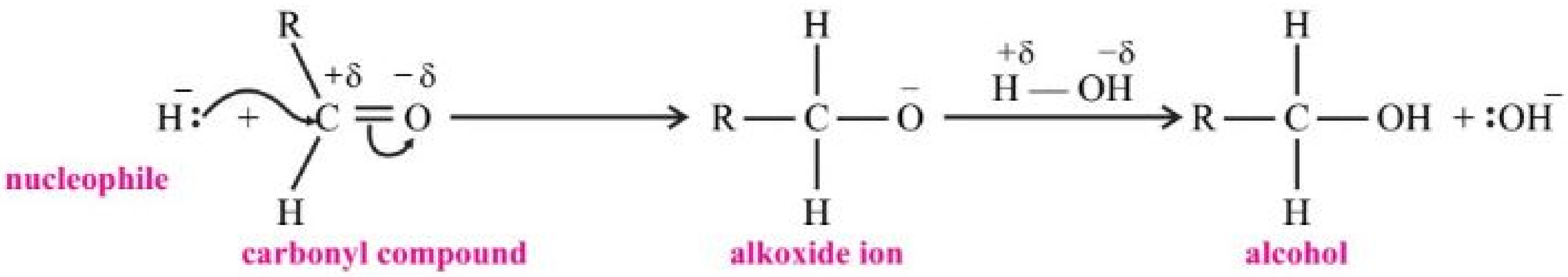
ethanol



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3+2[H]\xrightarrow[\text{alkalineaqucoussolution}]{NaBH_4\ Heat}CH_3-\overset{\overset{OH}{|}}{C}H-CH_3$$

propanone **propane-2-ol**

Mechanism



3. Addition of 2,4-Dinitrophenylhydrazine (Addition – elimination / Condensation Reaction)

Aldehydes or ketones undergo a condensation reaction with 2,4-dinitrophenylhydrazine (2,4-NDPH) to give an orange crystalline solids with well-defined melting points.

This reagent is used to identify carbonyl compounds. For example, ethanal reacts with 2,4-NDPH to form orange crystals of 2,4-dinitrophenylhydrazone. Other classes of organic compounds like carboxylic acids, esters, acyl halides, amides etc which also contain the carbonyl group $>C=O$ do not give this test.

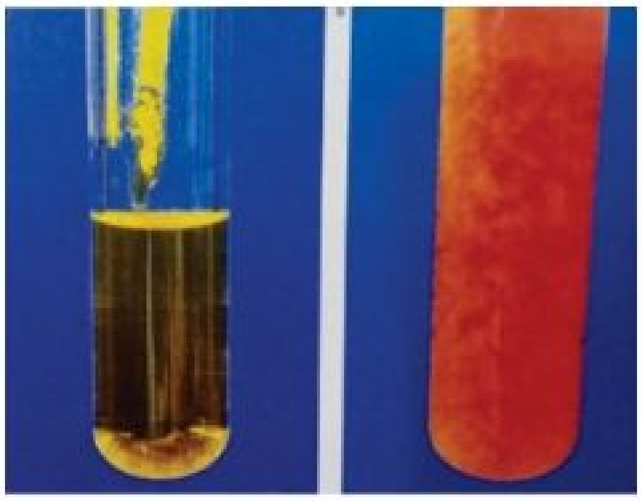


Figure 23.2: Ethanal gives orange crystalline 2,4-DNPH

23.3.2 Test of aldehydes and ketones

Aldehydes and ketones are oxidized to form carboxylic acids. Aldehydes are easily oxidized whereas ketones are reluctant towards oxidation because C-C bond has to be broken down during oxidation. Therefore, ketones are only oxidized by strong oxidizing agents, whereas aldehydes are oxidized by both weak and strong oxidizing agents.

i) Tollen's test

Tollen's reagent also called ammonical silver nitrate solution contains silver ions in aqueous alkaline solution. These silver ions are readily reduced to silver metal on gentle warming with an aldehyde. A silver mirror is formed along the wall of the test tube. A dilute solution of the glucose (aldehydic sugar) was used to make mirrors for domestic use by means of this reaction. Ketones do not give this test.

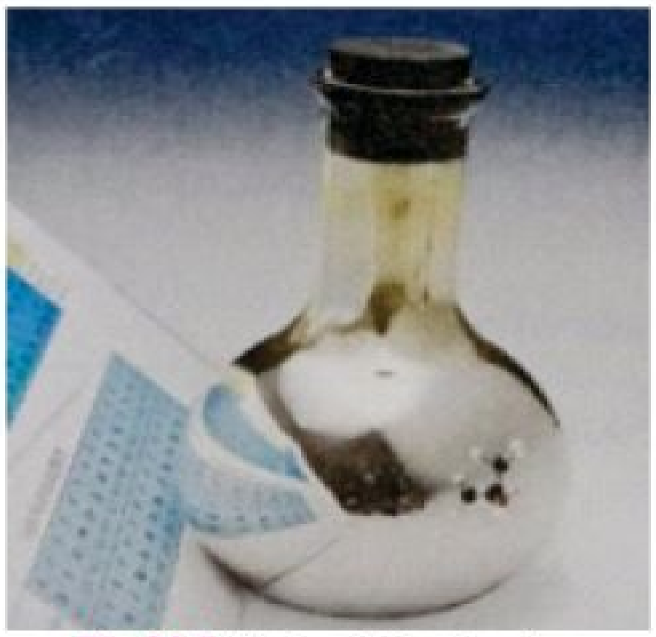
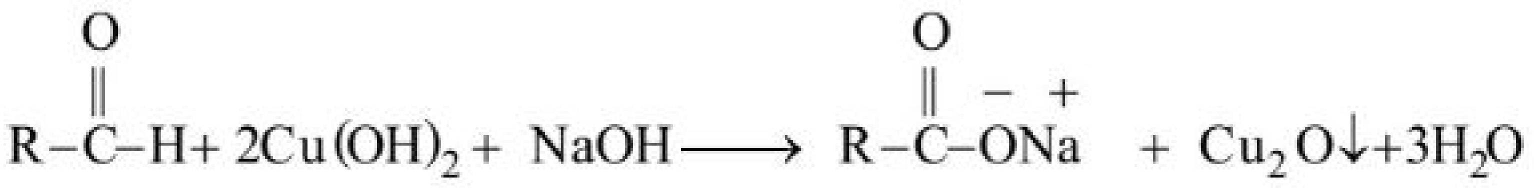


Fig.23.3 Only aldehydes give a positive Tollen's test

$$AgNO_3 + 3NH_4OH \longrightarrow [Ag(NH_3)_2]OH + NH_4NO_3 + 2H_2O$$

ii. Fehling's solution Test

Fehling's solution is the bright blue Fehling's solution of Cu^{2+} ions in an aqueous alkaline medium, complexed with salt of tartaric acid. When warmed with an aldehyde, the Cu^{2+} ions are reduced to Cu^{1+} ions, which in the alkaline solution form a brick-red precipitate of copper (I) oxide ketones do not give this test.

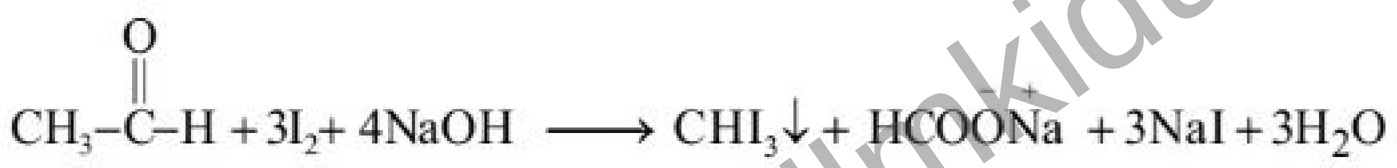


$$R-\overset{\overset{\Large O}{\|}}{C}-H + 2Cu(OH)_2 + NaOH \longrightarrow R-\overset{\overset{\Large O}{\|}}{C}-\overset{-}{O}\overset{+}{Na} + Cu_2O\downarrow + 3H_2O$$

iii. Iodoform Test

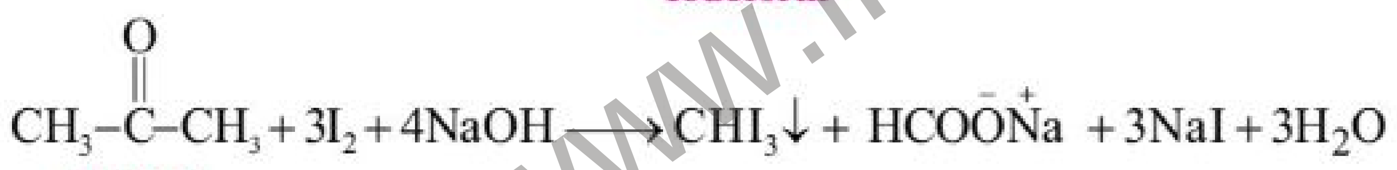
Aldehydes and ketones undergo substitution reactions by halogens readily at alpha position. Among aldehydes, only ethanal and among ketones, only methyl ketones possess the group CH_3CO- known as acetyl (ethanoyl) group. These compounds react with iodine in the presence of sodium hydroxide to form triiodomethane , a yellow crystalline solid called iodoform. Hence, the appearance of yellow precipitates will identify the presence of CH_3CO- group in the unknown carbonyl compound.

Aldehydes and Ketones having CH_3CO group, whereas alcohols having CH_3-CH(OH) group give iodoform test. Yellow coloured iodoform id formed in this reaction.



$$CH_3-\overset{\overset{\Large O}{\|}}{C}-H + 3I_2 + 4NaOH \longrightarrow CHI_3\downarrow + HCO\overset{-}{O}\overset{+}{Na} + 3NaI + 3H_2O$$

Ethanal **Iodoform**



$$CH_3-\overset{\overset{\Large O}{\|}}{C}-CH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3\downarrow + HCO\overset{-}{O}\overset{+}{Na} + 3NaI + 3H_2O$$

Acetone

Ethanol also gives this test, while methanol does not. The reason for this is the presence of CH_3-CH_2-O, which acts as a methyl ketone-like structure (CH_3-C=O).Thus it can also form iodoform, and the test is positive for ethanol.

$$CH_3CH_2OH + 4I_2 + 6NaOH \longrightarrow CHI_3 + HCOONa + 5NaI + 5H_2O$$

Quick Check 23.2

a) If compound A has the molecular formula C_3H_6O, it reacts with $NaBH_4$ to give compound B, C_3H_8O. Both A and B give a yellow precipitate with I_2/NaOH. Identify both compounds (A & B).

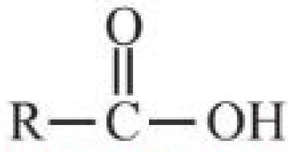
b) Why methanol does not give iodoform test while ethanol does?

c) Describe a test (a different one in each case) that you could use to distinguish between the following pairs of compounds. CH_3CH_2CHO

   i) CH_3CH_2 CHO and CH_3COCH_3
   ii) CH_3CH_2 $COCH_2CH_3$ and $CH_3CH_2CH_2COCH_3$
   iii) CH_2=CH–CH_2–OH and CH_3CH_2CHO

23.4 CARBOXYLIC ACIDS

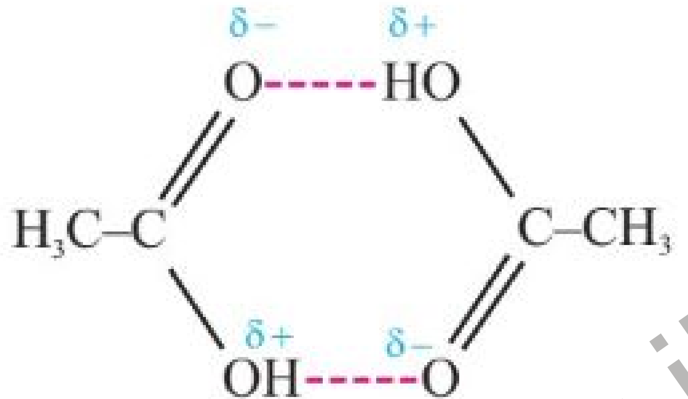
Carboxylic acids are the organic compounds having the carboxyl functional group (-COOH) in their molecules. The general structure of carboxylic acids is as below.



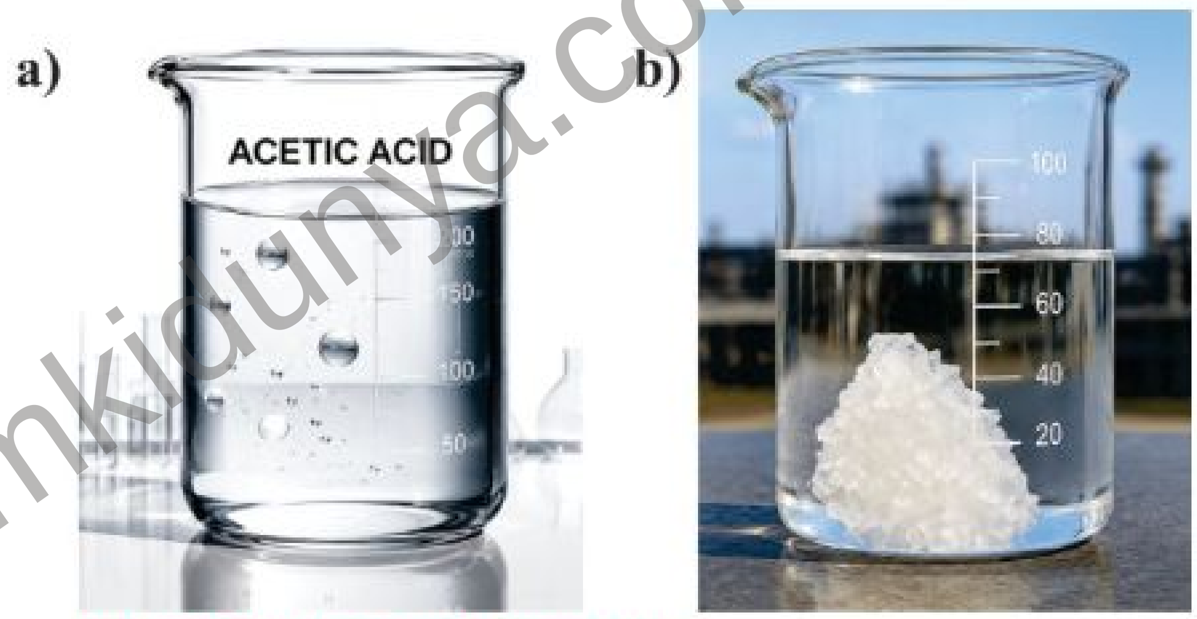
$$R-\overset{\overset{O}{\|}}{C}-OH$$

carboxylic acids

Common examples of carboxylic acids are methanoic acid (formic acid, found in ants) ethanoic acid (acetic acid, found in vinegar), and butanoic acid (butyric acid, in the rancid butter).
Lower carboxylic acids are generally liquids at room temperature, having high boiling points. This is due to their ability to make the hydrogen bond. The melting point of ethanoic acid is 17 °C, and its boiling point is 118 °C. The melting point of this acid is close to room temperature (25 °C), this is why it solidifies in winter. The solid form of pure ethanoic acid is called glacial acetic acid due to its resemblance with glaciers. Due to their ability to form the hydrogen bond, lower acids, i.e. methanoic acid and ethanoic acid are soluble in water.



Dimeric from of acetic acid formed due to the hydrogen bonding



Left: (a) acetic acid at room temperature
Right: (b) Glacial acetic acid at temperature below the room temperature

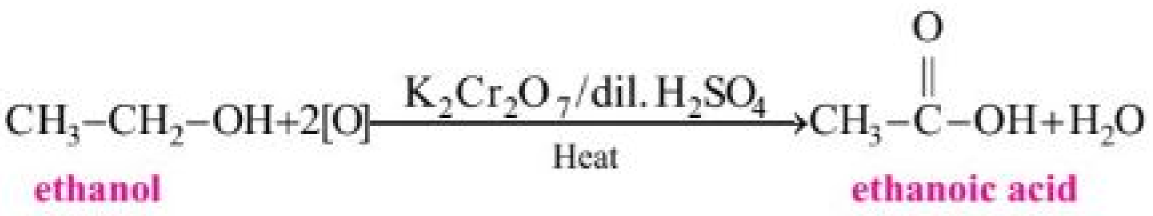
Long chain aliphatic monocarboxylic acids are called fatty acids. Stearic acid, palmitic acid, and oleic acid are found in vegetable oils in the form of triglycerides. They are insoluble in water due to their long hydrophobic alkyl chains.

23.4.1 Preparation of Carboxylic Acids

Carboxylic acids can be prepared by the following methods.

a) Oxidation of primary alcohols and aldehydes

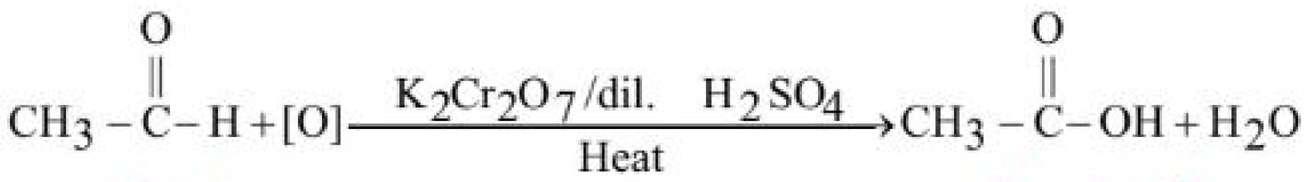
Carboxylic acids are prepared by the oxidation of primary alcohols and aldehydes. The starting material is refluxed with excess of either acidified $KMnO_4$ or acidified $K_2Cr_2O_7$.



$$CH_3-CH_2-OH+2[O]\xrightarrow[\text{Heat}]{K_2Cr_2O_7/\text{dil.}H_2SO_4}CH_3-\overset{\overset{O}{\|}}{C}-OH+H_2O$$

ethanol — ethanoic acid

Palmitic acid ($C_{16}H_{32}O_2$) is a long chain carboxylic acid found in palm oil in large quantities

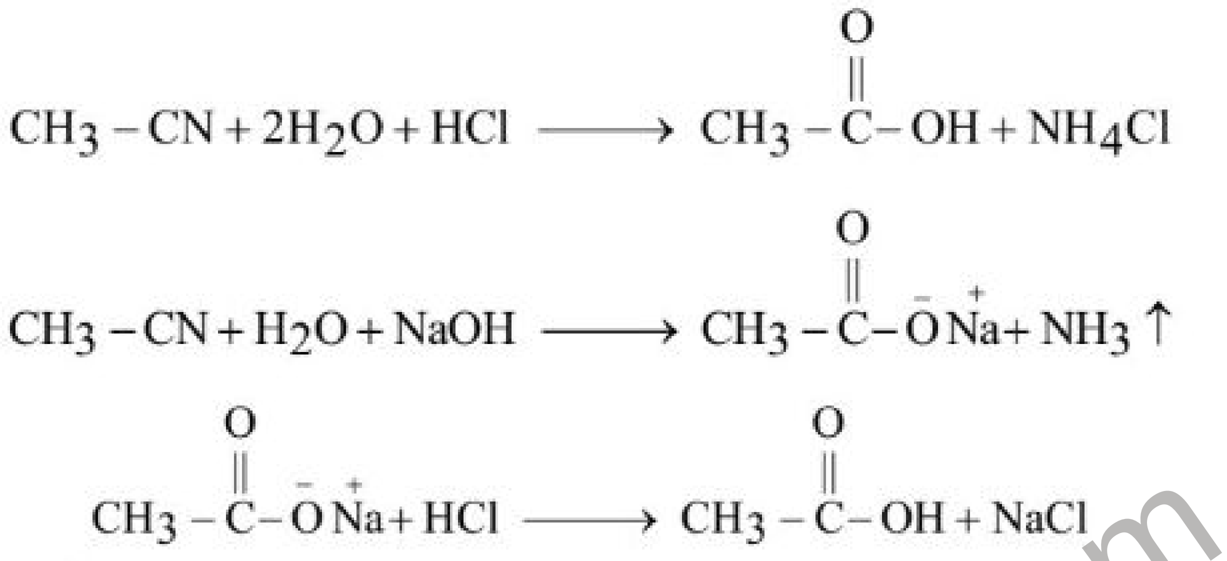


$$CH_3-\overset{\overset{O}{\|}}{C}-H+[O]\xrightarrow[\text{Heat}]{K_2Cr_2O_7/\text{dil. } H_2SO_4}CH_3-\overset{\overset{O}{\|}}{C}-OH+H_2O$$

ethanal **ethanoic acid**

b) Hydrolysis of alkane nitriles

Alkane nitriles can be directly hydrolysed to carboxylic acids in acidic medium. In alkaline hydrolyses, they first produce salts of carboxylic acids, which yield carboxylic acids on acidification.



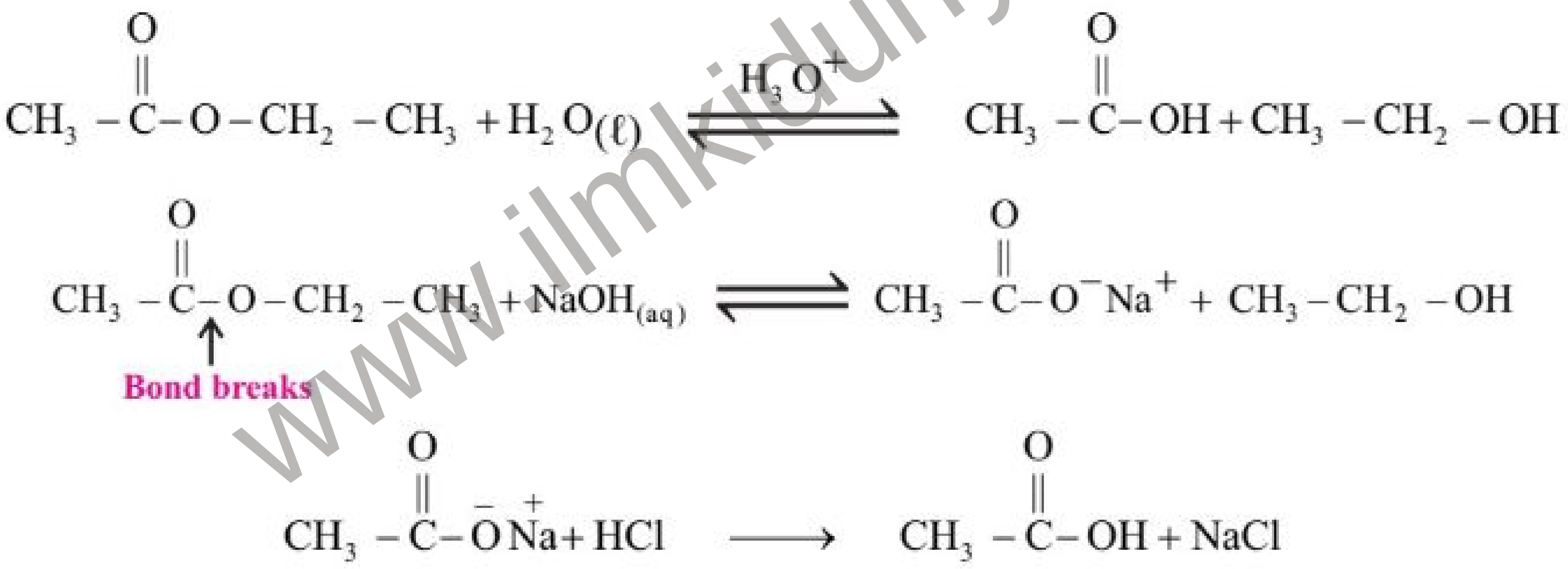
$$CH_3-CN+2H_2O+HCl\longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-OH+NH_4Cl$$

$$CH_3-CN+H_2O+NaOH\longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\overset{+}{Na}+NH_3\uparrow$$

$$CH_3-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\overset{+}{Na}+HCl\longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-OH+NaCl$$

c) Hydrolysis of esters

When an ester is refluxed with either dilute acid or dilute alkali, the ester is hydrolyzed to carboxylic acid or carboxylate ion.



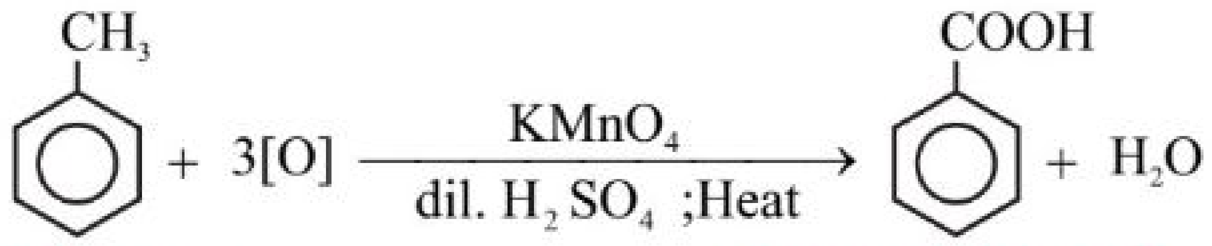
$$CH_3-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3+H_2O_{(\ell)}\overset{H_3O^+}{\rightleftharpoons}CH_3-\overset{\overset{O}{\|}}{C}-OH+CH_3-CH_2-OH$$

$$CH_3-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3+NaOH_{(aq)}\rightleftharpoons CH_3-\overset{\overset{O}{\|}}{C}-O^-Na^++CH_3-CH_2-OH$$

$$CH_3-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\overset{+}{Na}+HCl\longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-OH+NaCl$$

d) Preparation of benzenecarboxylic acid (Benzoic acid)

Methyl benzene is readily oxidized by acidified $KMnO_4$ or $K_2Cr_2O_7$ to benzoic acid.



methylbenzene **benzene carboxylic acid**

Quick Check 23.3

a) Write the equation for the oxidation of propanol with acidified $K_2Cr_2O_7$?

b) What products you expect from following? Give the chemical equations.

I) Hydrolysis of CH_3CH_2CN ii) Oxidation of ethylbenzene iii) Hydrolysis of ethyl ethanoate

23.5 REACTIONS OF CARBOXYLIC ACIDS

Reactions of carboxylic acids can be divided into the following types.

i. Reactions involving the acidic hydrogen only.

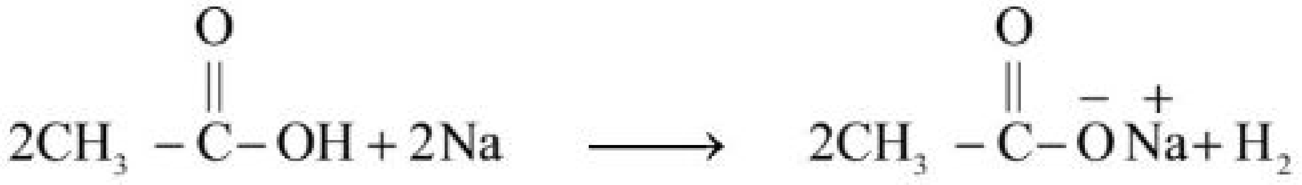
ii. Reactions involving the replacement of the –OH group.

iii. Those involving the carboxyl group as a whole.

A. Reaction involving acidic hydrogen

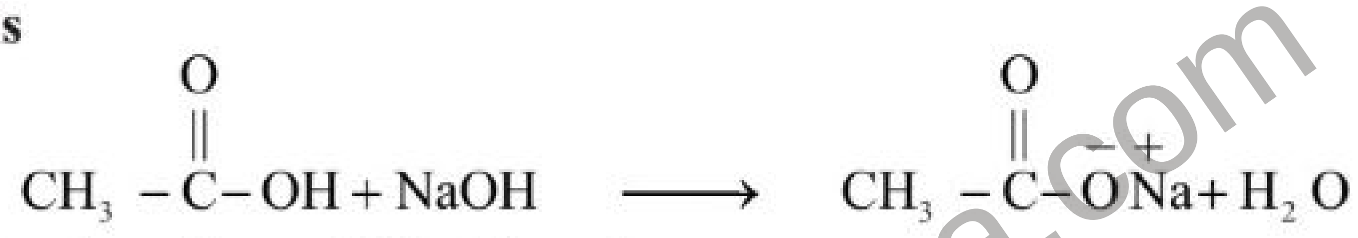
Carboxylic acids show considerable acidic character because they give H^+ ions in water. This why they can react with the basic species and active metals.

a) With active metals



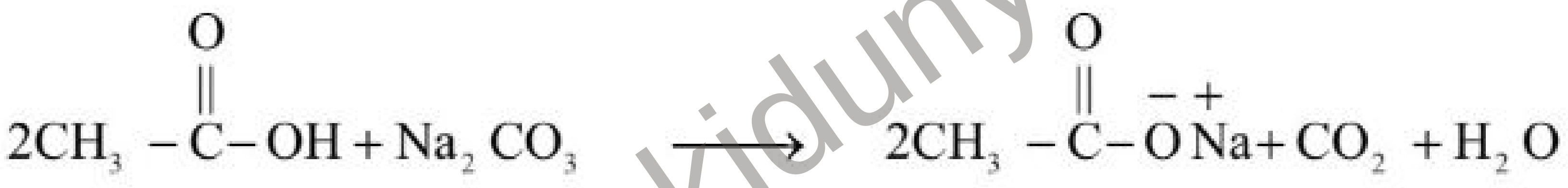
$$2CH_3-\overset{\overset{O}{\|}}{C}-OH+2Na \longrightarrow 2CH_3-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\overset{+}{Na}+H_2$$

b) With alkalis

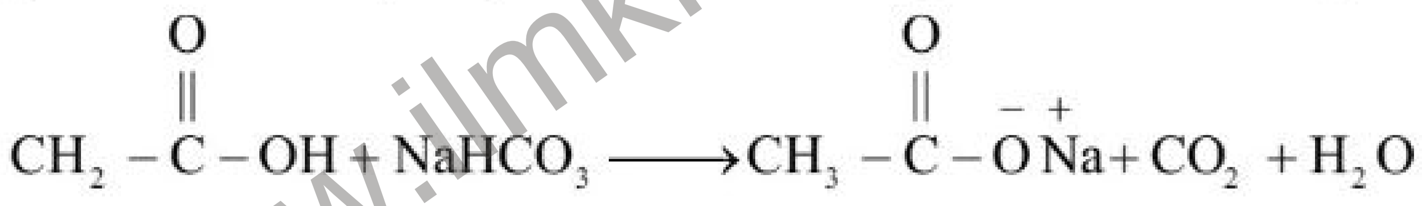


$$CH_3-\overset{\overset{O}{\|}}{C}-OH+NaOH \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\overset{+}{Na}+H_2O$$

c) With metal carbonates and bicarbonates



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

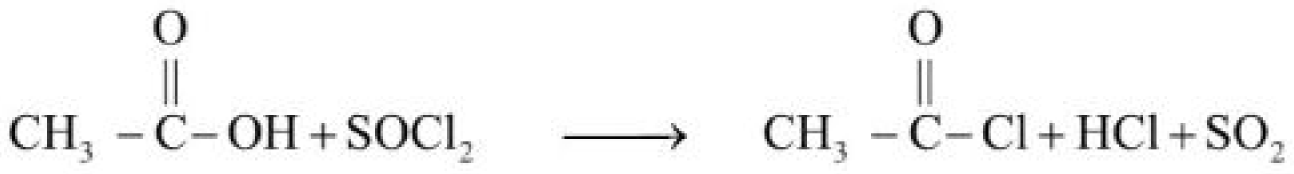


$$CH_2-\overset{\overset{O}{\|}}{C}-OH+NaHCO_3 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\overset{+}{Na}+CO_2+H_2O$$

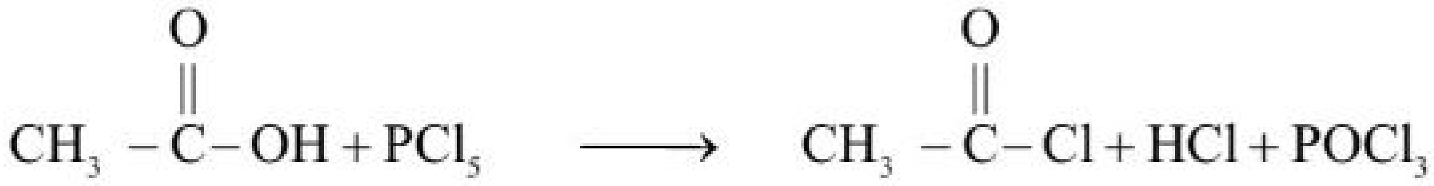
B. Reactions involving replacement of -OH group

Carboxylic acids can undergo substitution reactions in which the OH group is replaced by some other group like X, OR, NH_2 etc.

a) Reaction with $SOCl_2$, PCl_3 and PCl_5



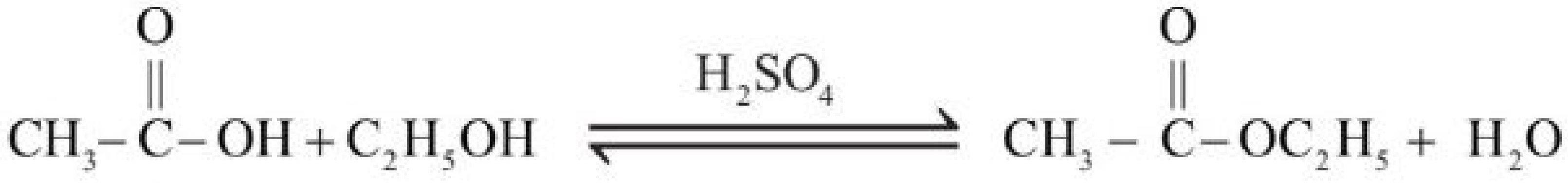
$$CH_3-\overset{\overset{O}{\|}}{C}-OH+SOCl_2 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-Cl+HCl+SO_2$$



$$CH_3-\overset{\overset{O}{\|}}{C}-OH+PCl_5 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-Cl+HCl+POCl_3$$

b) Reaction with alcohols (Esterification)

Carboxylic acids on heating with alcohols in the presence of concentrated sulphuric acid produce esters.



$$CH_3-\overset{\overset{O}{\|}}{C}-OH+C_2H_5OH \xrightleftharpoons{H_2SO_4} CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5+H_2O$$

ethanoic acid ethanol ethyl ethanoate

C. Reduction involving $-\overset{O}{\overset{\|}{C}}-OH$ group

The powerful reducing agent lithium tetrahydridoaluminate (III) reduces carboxylic acids to primary alcohols.

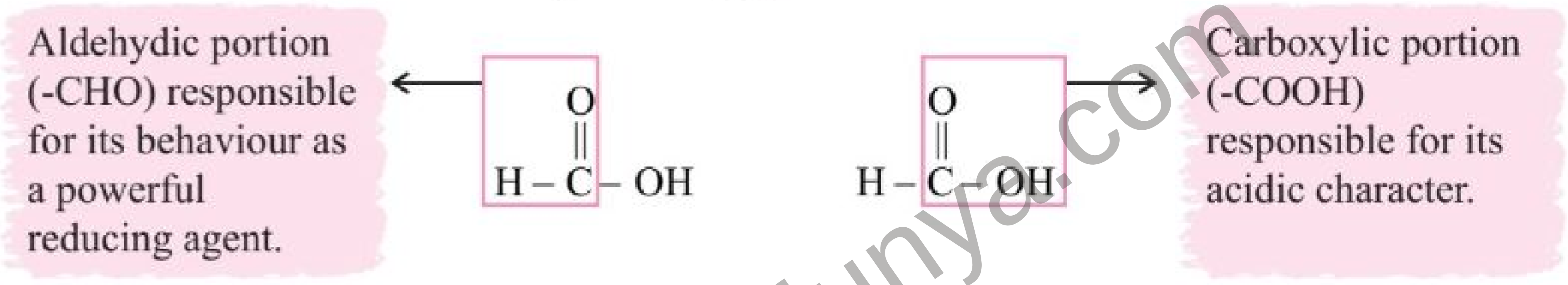
$$\underset{\text{ethanoic acid}}{CH_3-\overset{O}{\overset{\|}{C}}-OH} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{ethanol}}{CH_3-CH_2-OH} + H_2O$$

Reduction
i. Gain of H_2 (or H-)
ii. Loss of O or O_2
iii. Loss of X_2 (Halogens)
iv. Gain of electrons
v. Decrease in Ox state.

Other common reducing agents H_2/Ni and sodium tetrahydridoborate (III) will not reduce carboxylic acids.

Oxidation of carboxylic acids

Methanoic acid gets oxidized with both weak as well as strong oxidizing agents due to its structure and, hence, acts as a strong reducing agent.



Aldehydic portion (-CHO) responsible for its behaviour as a powerful reducing agent.

$H-\boxed{\overset{O}{\overset{\|}{C}}}-OH$ $\quad$ $H-\boxed{\overset{O}{\overset{\|}{C}}-OH}$

Carboxylic portion (-COOH) responsible for its acidic character.

Methanoic acid is the only monocarboxylic acid which gives positive silver mirror test (Tollen's test) and brick red precipitates with Fehling's solution. These reactions are used for the identification of methanoic acid.

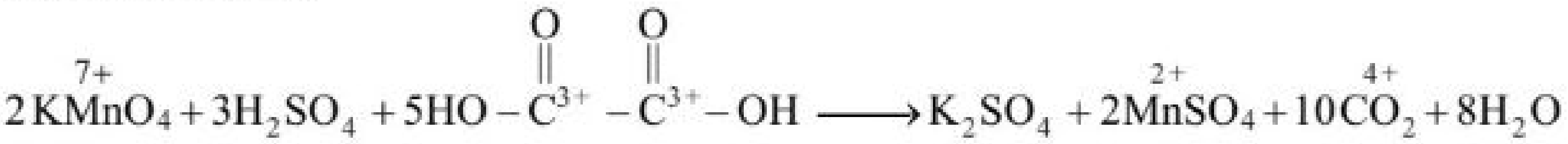
$$H-\overset{O}{\overset{\|}{C}}-OH + 2\left[Ag(NH_3)_2\right]OH \longrightarrow 2Ag\downarrow + CO_2 + 4NH_3 + 2H_2O$$

$$H-\overset{O}{\overset{\|}{C}}-OH + 2Cu(OH)_2 \longrightarrow Cu_2O\downarrow + CO_2 + 3H_2O$$

(brick red ppt)

Oxidation
1. Loss of H_2 or (H^-)
2. Addition of O or O_2
3. Addition of X_2
4. Loss of electrons
5. Increase in Ox. State

The oxidation of ethanedioic acid with acidified $KMnO_4$ or $K_2Cr_2O_7$ results in the formation of carbon dioxide and water.

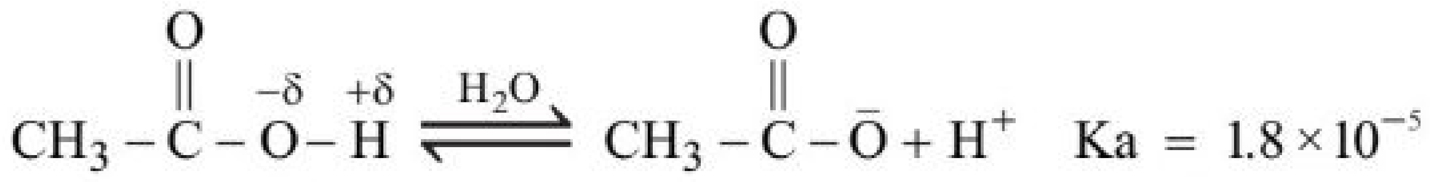


$$2K\overset{7+}{Mn}O_4 + 3H_2SO_4 + 5HO-\overset{O}{\overset{\|}{C^{3+}}}-\overset{O}{\overset{\|}{C^{3+}}}-OH \longrightarrow K_2SO_4 + 2\overset{2+}{Mn}SO_4 + 10\overset{4+}{C}O_2 + 8H_2O$$

23.6 RELATIVE ACIDITIES OF CARBOXYLIC ACIDS

Carboxylic acids are considerably more acidic than phenols and phenols are even more acidic than alcohols. The relative values of acidity constant or ionization constant, Ka, are given below (table) for a carboxylic acid, phenol or an alcohol.

The acidic strength i.e, extent of ionization of an acid depends upon the stability of its conjugate base. For example,



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{-\delta}{O}-\overset{+\delta}{H} \xrightleftharpoons{H_2O} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\bar{O}+H^+ \quad Ka = 1.8\times10^{-5}$$

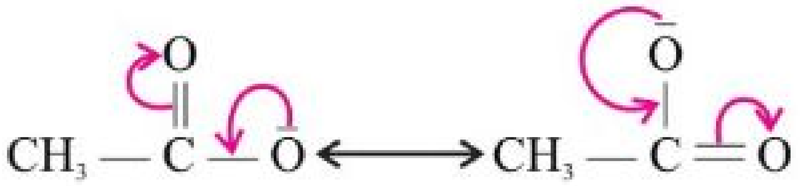
ethanoic acid ethanoate ion pKa = 4.76

Table 23.1

Substance	Ka	pKa
RCOOH	10^{-5}	5
ArOH	10^{-10}	10
HOH	10^{-14}	14
R-OH	10^{-16}	16

pKa=-log Ka
Higher the Ka or lower the pKa, stronger will be the acid and vice versa.

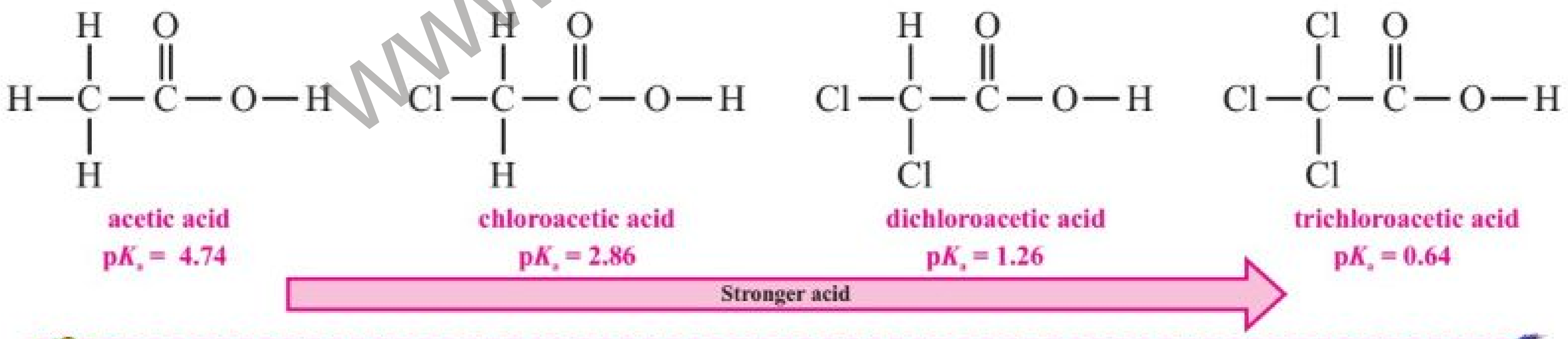
In the ethanoate ion (the conjugate base), the intensity of the negative charge on oxygen atom is decreased due to delocalization of electrons around the –COOH group. Due to this, the ethanoate ion becomes stabilized thus making it less likely to accept H^+ ions to form undissociated acid molecule.



The presence of an electron donating group (+I effect) will tend to destabilize the carboxylate ion by intensifying the negative charge and thus decreases the acidity of the acid. On the other hand, an electron withdrawing group (-I effect) will tend to stabilize the carboxylate ion by dispersing its negative charge and thus increases the acidity of the acid. For example, methanoic acid is 10 times stronger acid than ethanoic acid.

$$\underset{\text{(-1 effect)}}{\underset{\downarrow}{\boxed{H}}}-COOH \quad K_a = 1.8\times10^{-4} \quad pK_a = 3.75 \qquad \underset{\text{(+1 effect)}}{\underset{\downarrow}{\boxed{CH_3}}}-COOH \quad K_a = 1.8\times10^{-5} \quad pK_a = 4.75$$

For example, chloroacetic acid ($ClCH_2$-COOH) has a pK_a of 2.86, indicating that it is a stronger acid than ethanoic acid (pK_a = 4.74). Dichloroethanoic acid (Cl_2CH-COOH) is stronger, with a pK_a of 1.26. Trichloroacetic acid (Cl_3C-COOH) has a pK_a of 0.64, comparable in strength to some mineral acids.



acetic acid pK_a = 4.74 chloroacetic acid pK_a = 2.86 dichloroacetic acid pK_a = 1.26 trichloroacetic acid pK_a = 0.64

Quick Check 23.4

a) Methanoic acid is stronger than ethanoic acid. Give reason.

b) Place the following acids in order of strength, starting with the strongest acid first.

i) CH_3CH_2COOH ii) CH_3CCl_2COOH iii) $CH_3CHClCOOH$

c) Explain why ethanoic acid is a stronger acid than ethanol.

23.7 ESTERS

Esters are the derivatives of carboxylic acids that are obtained by their reactions with alcohols. Esters, unlike alcohols and carboxylic acids have no ability to form the hydrogen bond. This is why their boiling points are lower than the corresponding alcohols and carboxylic acids. The b.p of ethyl ethanoate ($CH_3COOC_2H_5$) is 77 °C, which shows its lower relative volatility compared to ethanoic acid and ethanol. Lack of hydrogen bonds makes esters less soluble/insoluble in water. Many esters are liquids with sweet fruity smells. Esters find many uses as solvents and flavouring agents in fruit drinks and sweets. Volatile esters are liquids with sweet fruity smells. Esters find many uses as solvents and flavouring agents in fruit drinks and sweets.

Fragrance of fruits and their tastes are due to esters

23.7.1 Preparations of Esters

Esters can be prepared by the following methods.

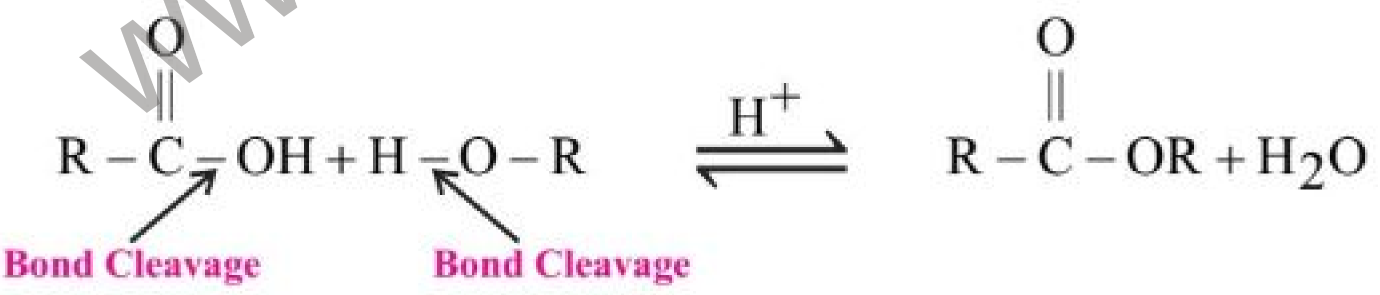
i. By the reaction of carboxylic acids and alcohol

The reaction of carboxylic acids with alcohols in acidic medium results in the formation of an ester. This reaction is known as Fischer's esterification. For example,

$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH+CH_3-CH_2-OH \xrightleftharpoons{H^+} CH_3-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3+H_2O$$

propanoic acid ethanol ethyl propanoate

In general



$$R-\overset{\overset{O}{\|}}{C}-OH+H-O-R \xrightleftharpoons{H^+} R-\overset{\overset{O}{\|}}{C}-OR+H_2O$$

Bond Cleavage Bond Cleavage

iii. By the reaction of acyl chlorides and alcohols

Acyl chlorides react vigorously with alcohols to form esters and their reactions go to completion and do not form an equilibrium mixture like the reaction between carboxylic acids and alcohols.

$$CH_3-\overset{\overset{O}{\|}}{C}-Cl+CH_3-CH_2-O-H \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3+HCl$$

ethanoyl chloride ethanol ethylethanoate

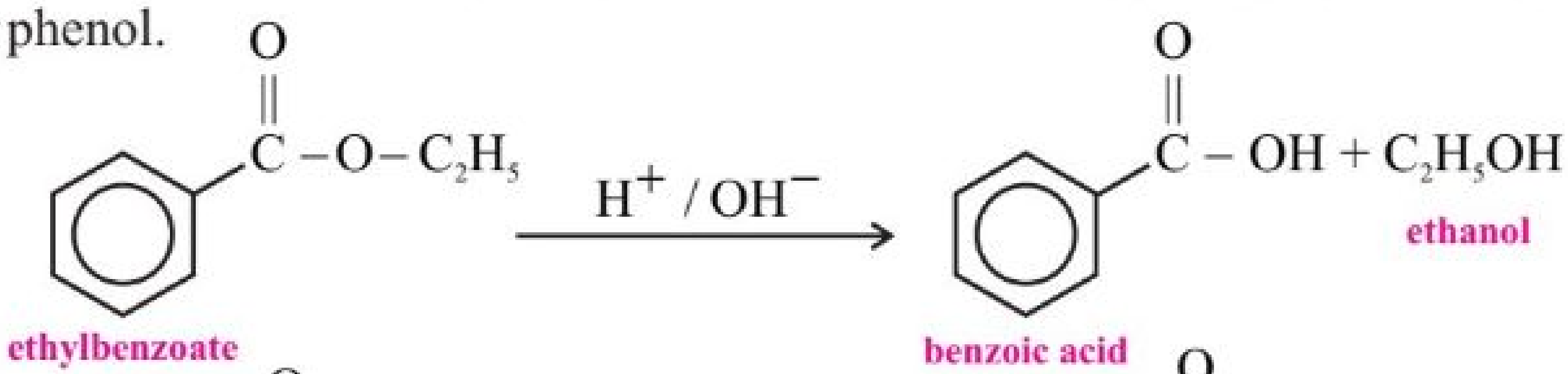
iv. By the reaction of acyl Chlorides and phenol

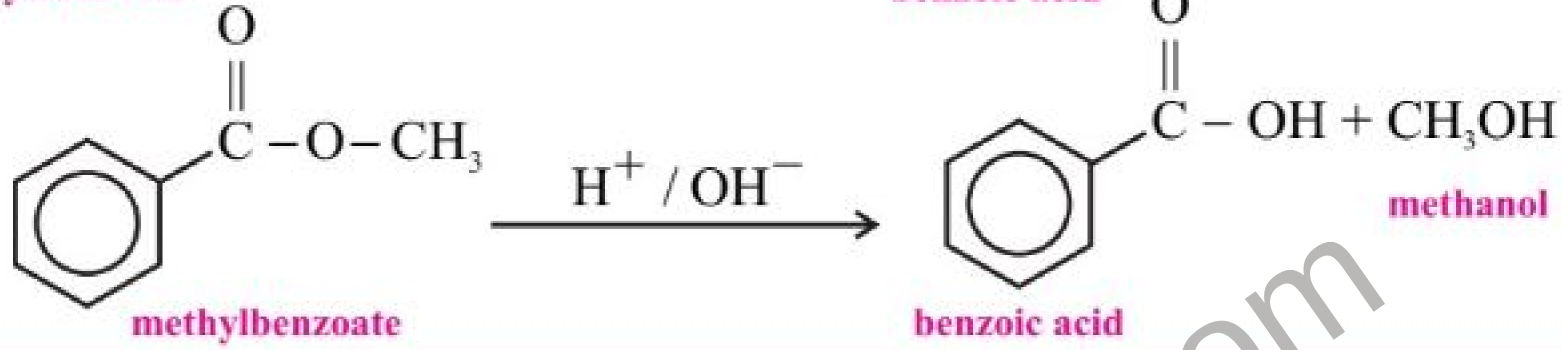
Phenyl esters are formed when acyl chloride is warmed with phenol. The reaction is already discussed in Chapter 22.

23.7.2 Reactions of Esters

i) Hydrolysis of esters

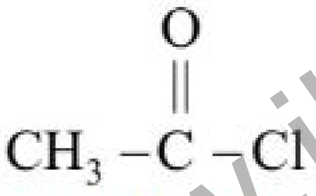
An ester is hydrolyzed slowly to a carboxylic acid and an alcohol (or a phenol). The reaction is either acid or base-catalyzed. The hydrolysis of aliphatic esters is already discussed earlier in this chapter. Aromatic esters are also hydrolysed in the same manner, giving aryl carboxylic acids and alcohols or phenol.





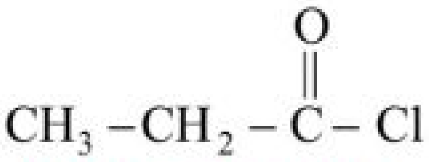
23.8 ACYL CHLORIDES

Acyl chlorides have the functional group $-\overset{O}{\overset{\|}{C}}-Cl$. Saturated aliphatic acyl chlorides have the general formula $C_nH_{2n+1}COCl$. According to the IUPAC system, they are named as alkanoyl halides. For example



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl$$

ethanoyl chloride



$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-Cl$$

propanoyl chloride

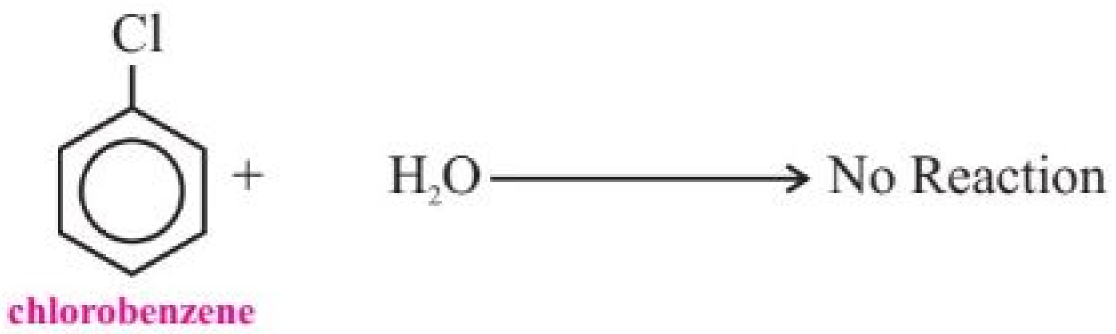
Since acyl chlorides are the most reactive compounds among the functional derivatives of carboxylic acids, they are usually prepared in such a way that they can be used for the preparation of other functional derivatives.

23.9 HYDROLYSIS OF ACYL CHLORIDES, ALKYL CHLORIDES AND ARYL CHLORIDES

The reactivity of acyl chlorides, alkyl chlorides and aryl (arene) chlorides can be compared with the ease of hydrolysis they undergo. Let us consider the following reactions.

$$\underset{\text{ethanoyl chloride}}{CH_3-\overset{O}{\overset{\|}{C}}-Cl} + H_2O \xrightarrow{\text{Room temperature, rapid}} \underset{\text{ethanoic acid}}{CH_3-\overset{O}{\overset{\|}{C}}-OH} + HCl$$

$$\underset{\text{chloroethane}}{CH_3-CH_2-Cl} + H_2O \xrightarrow{\text{Heat under reflux}} \underset{\text{ethanol}}{CH_3-CH_2-OH} + HCl$$



In ethanoyl chloride, the carbonyl carbon is having partial positive charge due to the strong electron withdrawing effect of two highly electronegative atoms: oxygen and chlorine directly attached to the carbon. Hence nucleophilic attack of H_2O on electrophilic carbon is so fast that reaction is completed within few minutes.

In ethyl chloride, the carbon gets comparatively less partial positive charge because it is attached to only chlorine atom. So, the nucleophilic attack of water is comparatively slow and takes 14 days to be completed even at 100°C.

On the other hand in chlorobenzene, the carbon bonded to chlorine is the part of benzene ring. Here, lone pair on chlorine participates in delocalization with π elections of the benzene ring. This will create a double bond character in C-Cl bond making it so strong that it will not break and, hence, does not take part in the chemical reaction.

Quick Check 23.5

a) Why do phenols not react directly with carboxylic acids to form phenyl esters?

b) Phenyl ethanoate is the ester responsible for the fragrance of peach and strawberry. It can be prepared from the ethanoyl chloride and phenol. Write down a chemical reaction for the preparation of this ester.

c) Predict the products of the following reactions, write the chemical equations.

I) Chlorobenzene and ethanol ii) Propanoyl chloride and phenol

Exercise

Q1. Multiple Choice Questions:

I. Ketones are prepared by the oxidation of alcohols:

a) Primary b) Secondary

c) Tertiary d) Quaternary

II. Which of the following will not give the iodoform test?

a) Acetaldehyde b) 2-pentanone

c) 3-Pentanoacid d) Acetone

III. When a carboxyl acid reacts with an alchol, the product is an:

a) Ethers b) Ester

c) Anhydride d) Amide

IV. Carboxylic acids react with carbonates to produce gas.

a) H_2
b) CO
c) CO_2
d) CH_4

V. Which type of alcohols produces aldehydes?

a) Primary
b) Secondary
c) Tertiary
(d) both a and b

VI. The hybridizalion of the oxygen of carbonyl group is:

a) sp
b) sp^2
c) sp^3
d) dsp^2

VII. Which is the main product of the reaction between acetic acid and PCl_5.

a) CH_3-Cl
b) CH_3COCl
c) HCl
d) $POCl_3$

VIII. Acidic character of chlorine substituted carboxylic acid is higher because chlorine is:

a) Electropositive
b) Electron with drawing due to –I
c) Electron donating due to +I
d) having three loan pairs

IX. When formic acid is oxidized, which of the following is formed?

a) water
b) carbon dioxide
c) carbon dioxide and water
d) carbon monoxide

X. The mechanism by which acyl chlorides react with alcohols is.

a) Addition
b) Elimination
c) Addition-elimination
d) Substitution

Q2. Attempt the following short answer questions:

a) How is ethanol converted to acetic acid?
b) Give the mechanism for the reductions of ethanal with $NaBH_4$.
c) What is iodofrom reaction?
d) Methanoic acid can be oxidized but other carboxylic acids cannot. Why?
e) Explain the influence of chlorine substitution on the acidity of carboxylic acids.
f) Give the reaction of acyl chloride with phenol.
g) Explain why carboxylic acid is more acidic than ethanol.
h) Give reaction of methanal with the Tollen's reagent.
i) Write down structural formulae of the following compounds.

i) 2-methylhexanal
ii) 2-methyl-3-pentanone
iii) 3-hydroxypentanl
iv) 4-nitro-2-pentanone
v) 2-chlorobutanol

Q3. CONSTRUCTED RESPONSE QUESTIONS:

a) Write down the equation for the reaction of $CH_{3.}CH_2$-CHO with $LiAlH_4$ (dry ether).

b) An alcohol, $C_4H_{10}O$ undergoes oxidation to form a carboxylic acid, $C_4H_8O_2$. Give a chemical equation along with conditions.

c) Write the structures of all the isomeric alcohols with formula $C_4H_{10}O$. Give their systematic names. Which one of them forms the above carboxylic acid? Explain why the others do not.

d) Propanoic acid can be reduced to propan-1-ol by reduction with $LiAlH_4$. Give a balanced chemical equation. Can we use $NaBH_4$ for this reaction? If not, give reason.

DESCRIPTIVE QUESTIONS:

Q4. What are aldehydes and ketones? Give the preparation of each.

Q5. Give four methods for the preparation of carboxylic acids.

Q6. How does ethanoic acid reacts with:

I) NaOH ii) ethanol

iii) SOCl iv) PCl_5

Q7. Give the mechanisms of the reactions of carbonyl compounds with:

i) HCN b) $NaBH_4$

Q8. Explain the relative acidities of chlorine substituted carboxylic acids.

Q9. Explain the relative ease of hydrolysis of acyl chlorides, alkyl chlorides and halogenoarenes.