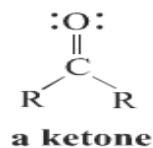
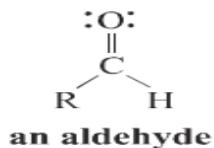
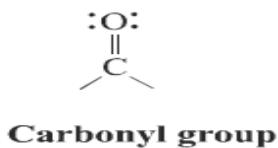


CHAPTER-12 ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

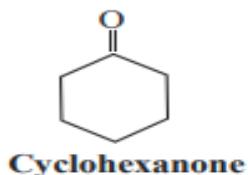
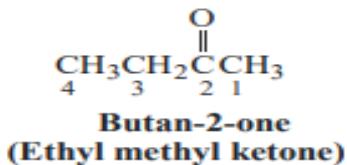
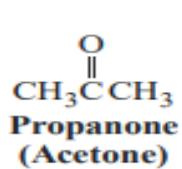
Both aldehydes and ketones possess the same general formula $C_nH_{2n}O$ and contain a common carbonyl ($>C=O$) group. In aldehydes, the carbonyl group is linked to an alkyl group and a hydrogen atom (except formaldehyde, having no alkyl group), while in ketones it is attached with two alkyl (aryl) groups (same or different).



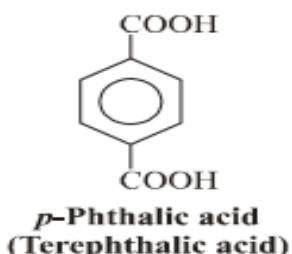
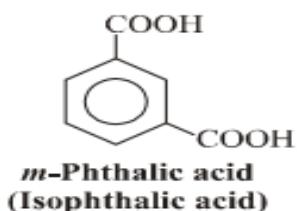
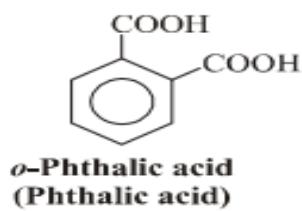
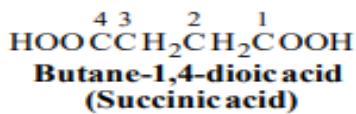
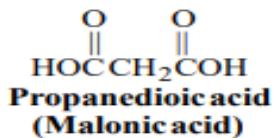
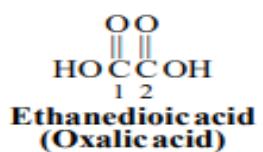
I Nomenclature:- In the IUPAC system of nomenclature, aliphatic aldehydes are named as alkanals. The final -e in the name of the corresponding alkane is substituted by -al. Note that when the -CHO group is attached to a ring, then the compound is called a carbaldehyde. Remember that the carbonyl carbon of the aldehydes is present at the end of the chain and is assigned 1 position. Therefore, it is not necessary to specify its position in the name of the aldehyde.



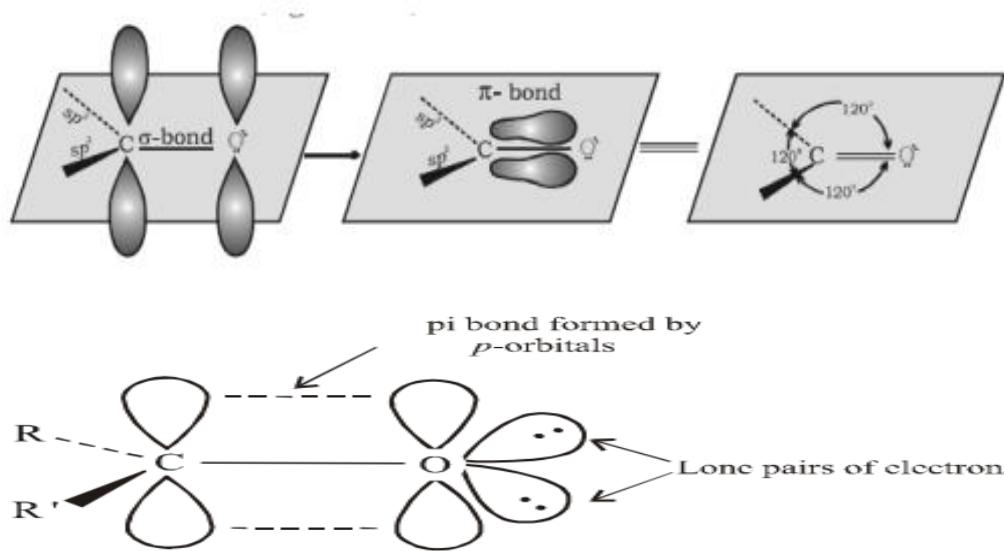
Ketones are named as alkanones in the IUPAC nomenclature. Their names are obtained by replacing final -e in the name of alkane by -one. The carbon chain is numbered in such a way that the carbonyl group gets the lowest number. Carboxylic acids are named by choosing the longest carbon chain containing the $-COOH$ group. The final -e in the name of the alkane is replaced by -oic acid



Carboxylic acids containing two carboxyl groups are called dicarboxylic acids. They are named by adding dioic acid as a suffix to the name of the corresponding hydrocarbon. Both the carboxyl carbon atoms are numbered as a part of the main chain. Note that in this case, final- e of the alkane is not dropped



II) Structure of the Carbonyl Group: The carbonyl carbon atom is sp^2 -hybridized and forms three sigma (σ) bonds. The fourth valence electron of carbon remains in its p-orbital and forms a π bond with oxygen by overlap with p-orbital of oxygen. In addition, the oxygen atom also has two nonbonding electron pairs. Thus, the carbonyl carbon and the three atoms attached to it lie in the same plane and the π -electron cloud is above and below this plane. The bond angles are approximately 120° as expected of a Trigonal coplanar structure



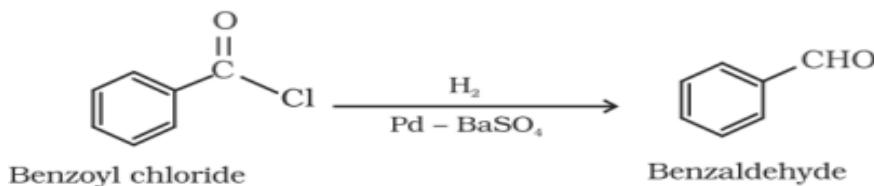
The structure of the carbonyl functional group

The oxygen atom, thus, acquires a partial negative charge (δ^-) whereas the carbon atom gets a partial positive charge (δ^+). This polar nature of the carbonyl group makes the oxygen atom nucleophilic and basic while the carbon atom becomes electrophilic. The physical properties and chemical reactions of aldehydes and ketones are a direct consequence of this polarisation.

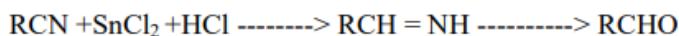
III) Methods of preparations for aldehydes and ketones (Carbonyl compounds)

- **From alcohols:** By controlled oxidation of 1° and 2° alcohols with acidified $K_2Cr_2O_7$ or $KMnO_4$ or MnO_2 or CrO_3 in CH_3COOH or chromic acid, H_2CrO_4 , in aqueous acetone or pyridinium chlorochromate (PCC) etc.

- **By catalytic dehydrogenation** of 1° and 2° alcohols over reduced copper heated to 300°C.
- Ketones can be obtained from 2° alcohols by oxidation with aluminium tert.-butoxide $[(CH_3)_3CO]_3Al$ Unsaturated 2° alcohols can also be oxidised to unsaturated ketones (without affecting the $>C=C<$) by this reagent.
- **From carboxylic acids:** By dry distillation of calcium “salts of fatty acids, e.g., calcium formate gives formaldehyde and calcium acetate gives acetone. An equimolar mixture of calcium acetate and calcium formate gives acetaldehyde.
- **From gem-dihalides :** By alkaline hydrolysis of terminal gem-dihalides, the aldehydes are formed, while non-terminal one give ketones
- **Hydroboration-oxidation:** Hydroboration (BH_3/HF) of terminal alkynes followed by oxidation with alk. H_2O_2 gives aldehyde, but non-terminal alkynes under similar conditions yield ketone.
- **From Grignard reagents:** On reaction with nitriles, i.e., Grignard reagents give aldehydes with HCN and ketones with RCN.
- **Rosenmund's reduction :** Acid chlorides can be reduced ~to aldehydes with" hydrogen in boiling xylene using Pd or Pt catalyst supported on BaSO₄. Ketones cannot be prepared by this method. The function of BaSO₄ is to poison the catalyst to prevent further reduction of aldehyde to 1° alcohol.

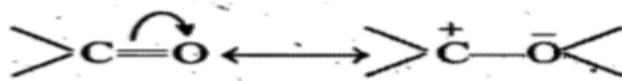


- **Stephen's reduction:** The reduction of alkyl cyanide by SnCl₂ and conc. HCl followed by acid hydrolysis to give aldehyde is known as Stephen's reaction



IV) Physical properties: Except HCHO (it is a gas), all other aldehydes and ketones are volatile liquids at ordinary temperature. Lower aldehydes have unpleasant odour while, ketones possess pleasant smell. The carbonyl compounds are strongly polar in nature which results in appreciable intermolecular attraction. Therefore, their boiling points are higher than those of non-polar substances of comparable molecular weights. However, their boiling points are lower than corresponding alcohols due to the absence of intermolecular hydrogen bonding.

V) Chemical properties: Both aldehydes and ketones contain a $>\text{C=O}$ group which is highly polar due to resonance and permanent -I effect of the negative oxygen atom.



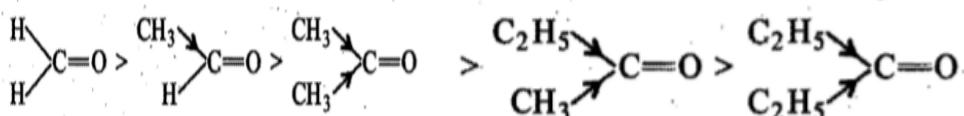
The positively charged carbon is readily attacked by the electron rich nucleophiles, while the negatively charged oxygen is attacked by electron deficient electrophiles.

➤ Relative reactivity of aldehydes and ketones

The reactivity of $>\text{C=O}$ group for nucleophilic addition depends mainly on

- Ability of carbonyl oxygen to carry a negative charge,
- Inductive effect of the groups attached to the carbonyl carbon atom and
- Size of substituent group (steric factor).

The decreasing order of reactivity of $>\text{C=O}$ group is as follows::



Thus, +I effect of alkyl group decreases the reactivity whereas the introduction of negative group (-I effect), increases the reactivity, e.g. chloral (trichloroacetaldehyde) is more reactive than acetaldehyde as the chlorine atoms increase the positive charge on the carbonyl carbon. The α -H atoms of aldehydes and ketones are reactive (acidic in nature). This is due to the fact that the anion resulting from removal of α -H atom by base gets stabilized by resonance.

➤ **Reactions common to aldehydes and ketones**

- Substitution reactions: The α -H atom of alkyl group of $>\text{C=O}$ compounds can be replaced by halogen atoms (Cl_2 or Br_2) even at room temperature. Acetaldehyde on halogenation (chlorination) gives trichloroacetaldehyde (chloral) and acetone yields trichloroacetone. The excess of alkali decomposes the trihalogen compounds to give haloform (CHX_3)
- Acetaldehyde, acetone and methyl ketones ($-\text{COCH}_3$) undergo haloform (Iodoform) reaction with X_2 (12) and NaOH .

➤ **Reactions of carbonyl group**

- (i) Addition of hydrogen:** Different products are obtained depending on the nature of reducing agents.

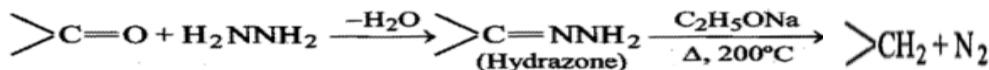
- Molecular hydrogen in presence of metallic catalyst (such as Ni, Pt and Pd) reduces aldehydes and ketones into 1° and 2° alcohols respectively.

- With nascent hydrogen produced (such as Zn + CH₃COOH, Na + C₂H₅OH, Na + H₂O, Zn + alc. NaOH, etc.) gives 1° and 2° alcohols (reduction to alcohols).
- With LiAlH₄, NaBH₄ or LiBH₄ (complex metallic hydrides), aldehydes give 1° alcohol while ketones give 2° alcohol.
- Unsaturated aldehydes can be reduced to unsaturated alcohols (1°) without affecting C=C in presence of reducing agents LiAlH₄ in dry ether or NaBH₄ in alcohol.

Clemmensen's reduction: Aldehydes and ketones are converted into alkanes, (i.e.,)C=O group is reduced to >CH₂ group) when treated with Zn-Hg and conc. HCl. This reaction is known as Clemmensen's reduction.

The same conversion (>C=O into CH₂) can be made by heating aldehydes and ketones with red P and conc HI

Wolff-Kishner reduction: Aldehydes and ketones are conveniently reduced to hydrocarbons in presence of excess of hydrazine (H₂N-, NH₂) and strong base (NaOH or C₂H₅ONa) on heating



(ii) **Addition of Grignard reagents:** The >C=O group adds onto Grignard reagent and the addition product on hydrolysis decomposes to yield 1°, 2° or 3° alcohol depending on the nature of carbonyl compound. For example, HCHO forms 1° alcohol, higher aldehydes (RCHO) give 2° alcohols and ketones give 3° alcohol.

(iii) **Reaction with thioalcohols:** Thioalcohols react more rapidly than alcohols and form thioacetals and thioketals. Replacement of carbonyl oxygen (Condensation reactions)

(iv) **Aldol condensation (Reactions involving α-hydrogen):** It is a chemical reaction in which two or more molecules of same or different carbonyl compounds containing α -H atoms unite together in the presence of a dilute base such as NaOH, Ba(OH)₂ or K₂CO₃ etc., to form a new product which combines the properties of alcohol and aldehyde or ketone, is called aldol condensation

➤ Reactions in which aldehydes and ketones differ

- Oxidation of aldehydes:** Aldehydes are easily oxidised to corresponding carboxylic acids and thus acts as strong reducing agents. Oxidising agents may be strong (such as acidified K₂Cr₂O₇ or acidified Na₂Cr₂O₇ or acidified KMnO₄ or hot conc. RN₃) or mild (such as Tollens' reagent or Fehling's solution or Benedict's solution).
- Reduction of Tollens' reagent:** It is ammoniacal AgNO₃. Aldehydes reduce weak (mild) oxidising agents like ammoniacal AgNO₃ (Tollens' reagent) to metallic silver which deposits as mirror (Reducing character of aldehydes). This reaction is known as silver mirror test.
- Reduction of Fehling's solution:** It is an alkaline solution of cupric ion complexed with sodium potassium tartrate. Aldehydes on heating with Fehling's solution give a reddish brown precipitate of cuprous oxide (Cu₂O).

- **Schiff's test of aldehydes:** Schiff's reagent is a dilute solution of p-rosaniline hydrochloride whose pink (red) colour has been discharged by passing SO_2 gas. Aldehydes when treated with Schiff's reagent (magenta solution in H_2SO_3) restore its pink colour. Ketones do not give this test.
- **Cannizzaro's reaction:** HCHO , $\text{C}_6\text{H}_5\text{CHO}$ and other aldehydes containing no α -hydrogen atoms on heating with conc. alkali solution undergo oxidation reduction reaction. In this reaction, one molecule of aldehyde is oxidised to carboxylic acid and the other is reduced to 1° alcohol (disproportionation). This is known as Cannizzaro's reaction.

CARBOXYLIC ACIDS

Organic compounds containing carboxylic (-COOH) functional group are called carboxylic acids. The -COOH group has its own distinctive properties and has no relation with) $\text{C}=\text{O}$ and -OH compounds.

I) General methods of preparation

By Oxidation of alcohols, aldehydes and ketones:

Using oxidising agents $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ (dil.) or alkaline KMnO_4 or air in presence of catalyst. Aldehyde can be oxidised to corresponding carboxylic acid even with mild oxidising agents such as ammonical AgNO_3 {Tollens' reagent).

By hydrolysis of alkane nitriles: Compounds containing a~ group can be hydrolysed to -COOH group in presence of H^+ (HCl or H_2SO_4) or with alkali.

By carbonation of Grignard reagents: When CO_2 (solid ice) is passed through an ethereal solution of $\text{R}-\text{MgX}$, an addition product is formed which on hydrolysis with a mineral acid yields a carboxylic acid

From alkenes (By carbonylation): A mixture of an alkene, CO and steam is heated under pressure at 350°C in presence of catalyst H_3PO_4 , monocarboxylic acid is formed. Ketones react with Mg-Hg over water gives carboxylic acid. This reaction is called **Koch reaction**.

Acidity of carboxylic acids

- The acidic character decreases with the rise of molecular weight. HCOOH is the strongest acid of all fatty acids. Thus, the acidity of carboxylic acid is due to powerful resonance stabilization of the anion.

- Electron attracting group (-I effect) stabilises the anion and therefore increases ionization of the acid. The greater is the -I effect, greater will be the acidic strength,

i.e., $\text{Cl}_3\text{CCOOH} > \text{Cl}_2\text{CHCOOH} > \text{ClCH}_2\text{COOH} > \text{CH}_3\text{COOH}$ and $\text{FCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{BrCH}_2\text{COOH} > \text{ICH}_2\text{COOH}$ (because $\text{F} > \text{Cl} > \text{Br} > \text{I}$).

- Electron releasing group (+I effect) destabilises the anion and so decreases the acidity.

i.e. $\text{HCOOH} > \text{CH}_3\text{COOH} > \text{CH}_3\text{CH}_2\text{COOH} > (\text{CH}_3)_2\text{CHCOOH} > (\text{CH}_3)_3\text{C-COOH}$

Chemical properties

(1) Reactions due to -C-OH group

(a) Reactions involving proton (removal of H-atom of -OH group):

Salt formation: Monocarboxylic acids react with Na, K, NaOH, NaHCO₃ or Na₂CO₃ etc. with the evolution of hydrogen and form corresponding salt.

Reaction with organometallic reagents: R'COOH reacts with RMgX (GR) rapidly to give an alkane (RH) corresponding to the alkyl group of Grignard reagent.

(b) Reactions involving -OH group:

Ester formation: RCOOH reacts with ROH in presence of dehydrating agents like conc. H₂SO₄ or dry HCl gas to form esters.

Formation of acid chlorides: By the action of PCl₅/PCl₃, SOCl₂/pyridine or Cl₂/Br₂ in presence of red P on carboxylic acids, acid halides are formed.

Formation of acid anhydrides: Dehydration of monocarboxylic acids on heating with P₂O₅ gives acid anhydride or when sodium salt of acid is heated with acid chloride, acid anhydrides are formed.

Formation of amides and nitriles: Monocarboxylic acids on treatment with NH₃ form ammonium salts which on heating lose a molecule of water to form corresponding amides

(c) Reactions involving (carbonyl) group:

Reduction to alcohols: Reduction products depend on the nature of reducing agent. By using LiAlH₄ (LAH) in ether solution or ruthenium (Ru) and carbon as catalyst, the -COOH group is reduced to -CH₂OH (1⁰ alcohol). BH₃/THF or H₂ in presence of copper chromite (CuO + Cr₂O₃) also reduces -COOH into -CH₂OH

(d) Reactions involving -COOH group as a whole:

Decarboxylation: On heating anhydrous salt of acid with sodalime forms an alkane with the elimination of CO₂. When sodium formate is heated with sodalime, hydrogen is evolved.

By Kolbe's electrolytic reaction: Electrolysis of Na or K salts (concentrated aqueous solution) of fatty acids yields alkanes.

Reduction to alkanes: On heating with conc. HI and red P at 200°C or catalytic reduction, the -COOH converts into -CH₃ to form an alkane.

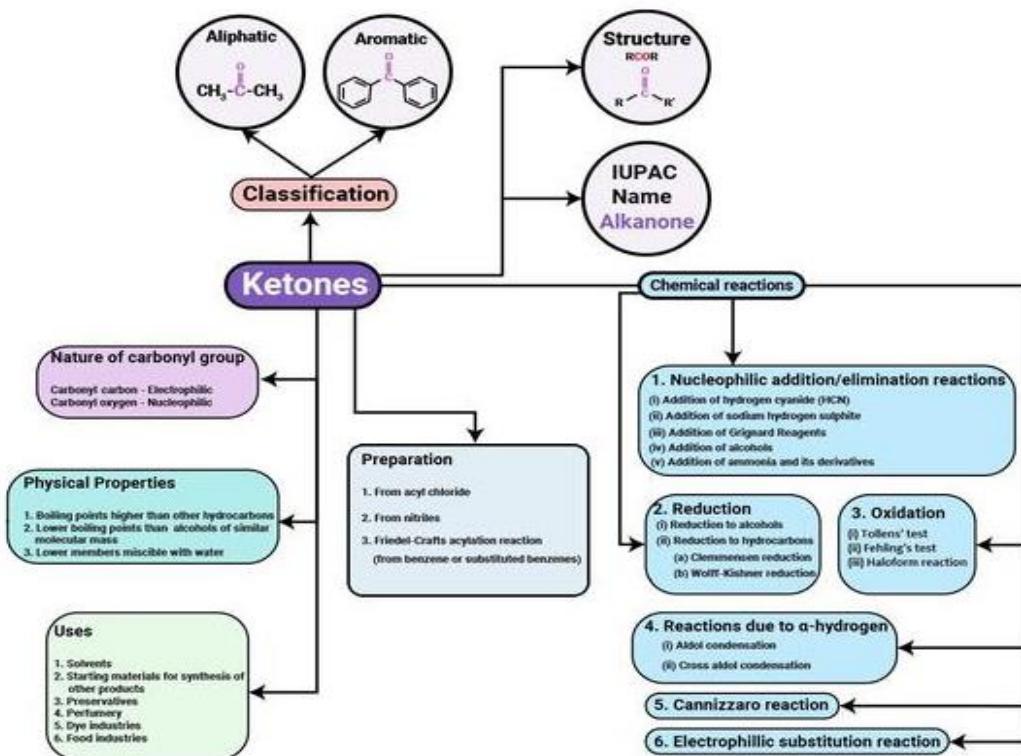
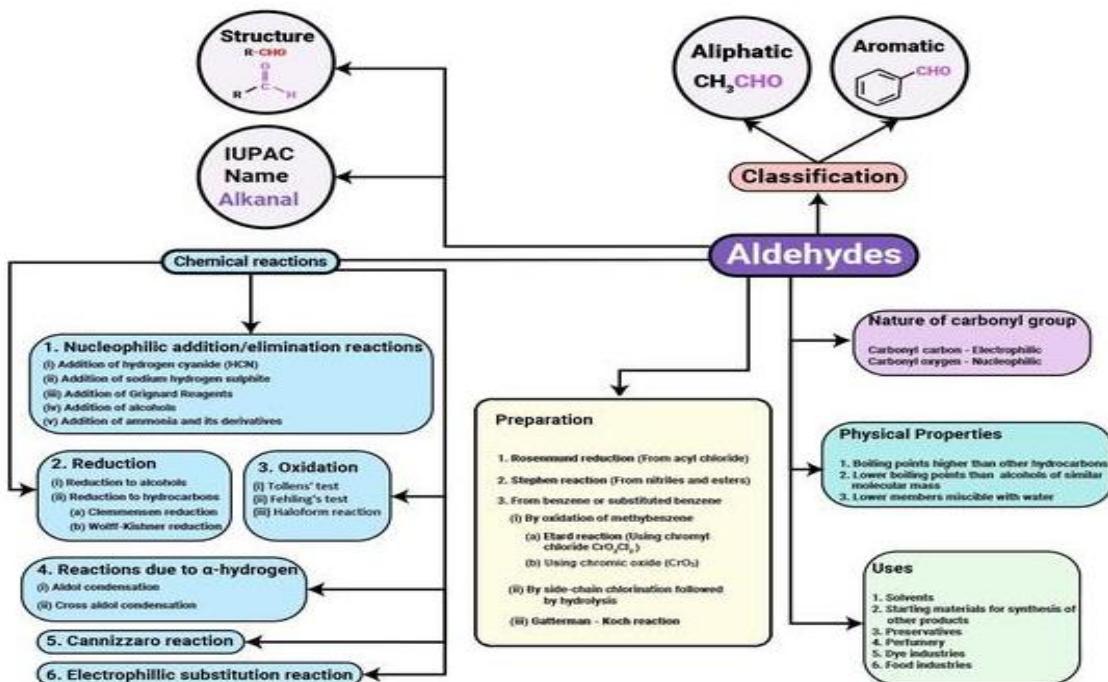
(2) Reactions due to R (alkyl) group

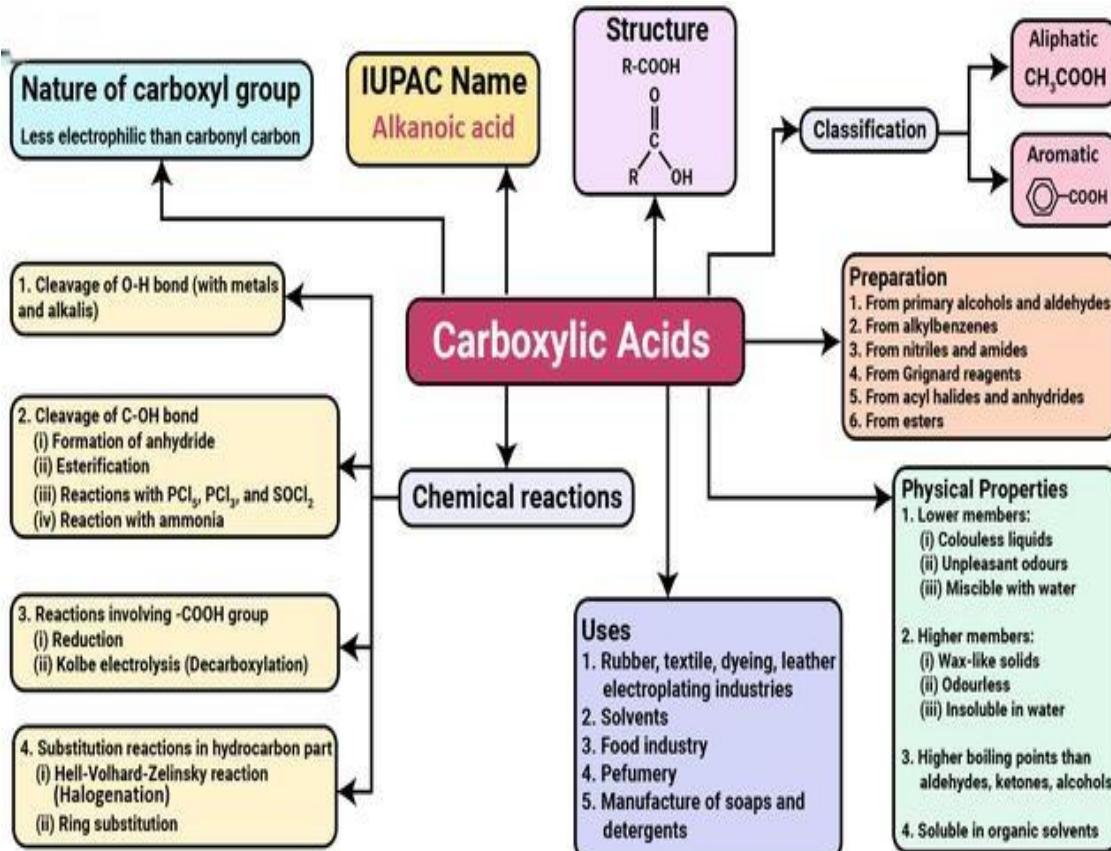
Halogenation: The α -hydrogen atoms are highly reactive due to the presence of electronegative -COOH group. On halogenation (Cl₂ or Br₂) in presence of a catalyst (red P or Fe, etc.,), the α -H atoms are replaced by chlorine or bromine atoms. The reaction occurs in presence of sunlight or on boiling. This reaction is known as **Hell-Volhard-Zelinsky (HVZ) reaction**.

Direct iodination can be done in presence of an oxidising agent like HI₀₃ or HgO.

Oxidation : Carboxylic acids having at least one β -hydrogen convert into β -hydroxy carboxylic acids on oxidation with H₂O₂. Oxidation of α -methylene group takes place by SeO₂ to give α -keto acid.

MIND MAPS





TESTS OF ALDEHYDES AND KETONES (Distinction)

Tests	Aldehydes	Ketones
1. With Schiff's reagent	Give pink colour.	No colour.
2. With Fehling's solution	Give red precipitate.	No precipitate is formed.
3. With Tollen's reagent	Black precipitate of silver or silver mirror is formed.	No black precipitate or silver mirror is formed.
4. With saturated sodium bisulphite solution in water	Crystalline compound (colourless) is formed.	Crystalline compound (colourless) is formed.
5. With 2,4-dinitrophenylhydrazine	Orange-yellow or red well defined crystals with melting points characteristic of individual aldehydes.	Orange-yellow or red well defined crystals with melting points characteristic of individual ketones.
6. With sodium hydroxide	Give brown resinous mass (Formaldehyde does not give this test).	No reaction.
7. With sodium nitroprusside and few drops of sodium hydroxide	A deep red colour (Formaldehyde does not respond to this test).	Red colour which changes to orange.

OBJECTIVE TYPE QUESTIONS(MCQ)

1. When a mixture of calcium acetate and calcium formate is heated. It yields:
(a) acetone (b) acetaldehyde (c) formic acid (d) acetic acid
2. Which of the following compounds, is oxidised to prepare ethyl methyl ketone?
(a) Propan-2-ol (b) Butan-1-ol (c) Butan-2-ol (d) Tert. butyl alcohol
3. The reagent with which both acetaldehyde and acetone react easily is
(a) Fehling's solution (b) Grignard reagent (c) Schiff's reagent (d) Tollens' reagent
4. A compound that gives a positive iodoform test is:
(a) pentan-1-ol (b) pentan-2-one (c) pentan-3-one (d) pentanal
5. Schiff's reagent is:
(a) magenta solution decolourised with sulphurous acid
(b) magenta solution decolourised with chlorine
(c) ammoniacal cobalt chloride solution
(d) ammoniacal manganese sulphate solution
6. When acetaldehyde is heated with Fehling's solution, it gives a red precipitate of:
(a) Cu (b) CuO (c) CuSO₄ (d) Cu₂O
7. Hydrocarbons are formed when aldehydes and ketones are reduced with amalgamated zinc and conc. HCl. The reaction is called:
(a) Dow reduction (b) Clemensen's reduction
(c) Cope reduction (d) Wolff-Kishner reduction
8. The formation of cyanohydrin from a ketone is an example of:
(a) Electrophilic addition (b) nucleophilic addition
(c) Nucleophilic substitution (d) electrophilic substitution
9. Acetone is mixed with bleaching powder to give:
(a) Ethanol (b) acetaldehyde (c) chloroform (d) phosgene
10. Ketones react with Mg-Hg over water gives:
(a) alcohols (b) pinacols (c) pinacolones (d) none of these
11. Which of the following is not a fatty acid?
(a) Stearic acid (b) Palmitic acid (c) Propionic acid (d) Phenyl acetic acid
12. Formic acid and formaldehyde can be distinguished by treating with:
(a) Benedict's solution (b) Tollens' reagent
(c) Fehling's solution (d) NaHC₃O₃
13. Methyl magnesium bromide on reaction with SO₂ followed by hydrolysis gives
(a) methyl sulphonic acid (b) methane sulphonic acid (c) dithio acetic acid (d) ethanethiol

14. Oxalic acid on treatment with conc. H₂S0₄ gives:

- (a) CO only (b) CO₂ only (c) CO₂ + H₂O (d) H₂O+CO+C0₂

15. Propionic acid with Br₂/P yields a dibromo product. Its structure would be:

- (a) CH₂BrCH₂COBr (b) CH₂BrCHBrCOOH
(c) CHBr₂CH₂COOH (d) CH₃CBr₂COOH

ASSERTION REASON TYPE QUESTIONS: -

Following questions consist of an Assertion (A) and the Reason (R). Use the following keys to choose the appropriate answer:

- (a) If both (A) and (R) are correct and (R) is the correct explanation of (A)
(b) If both (A) and (R) are correct but (R) is not the correct explanation of (A)
(c) If (A) is correct but (R) is incorrect.
(d) If (A) is incorrect but (R) is correct.

1. (A) Carbonyl compounds take part in nucleophilic addition reactions.

(R) These reactions are initiated by nucleophilic attack' at the electron deficient carbon atom.

2. (A) Primary alcohols can be easily oxidized to aldehyde.

(R) Aldehydes are prone to further oxidation to carboxylic acids

3. (A) The addition of ammonia derivatives on carbonyl compounds is carried in weakly acidic medium. (R) In the weakly acidic medium, attacking nucleophile-is also protonated.

4. (A) Fehling's reagent is a test for all aliphatic aldehydes.

(R) Aliphatic aldehydes can be easily oxidised even with mild oxidising agents.

5. (A) 2-Methyl propanal undergoes Canniziaro's reaction.

(R) It has an alpha-hydrogen atom.

6. (A) Formaldehyde is a planar molecule.

(R) Carbon atom in formaldehyde is sp² -hybridised.

7. (A) Nitromethane can give aldol condensation.

(R) alpha-hydrogen of nitromethane is acidic.

8. (A) Chloral hydrate is stable.

(R) It is stable due to its high molecular weight.

9. (A) Acetaldehyde does not show aldol condensation.

(R) Compounds having at least one alpha-hydrogen give aldol condensation.

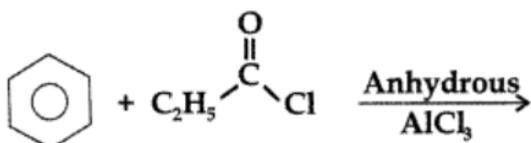
10. (A) Lower aldehydes and ketones are soluble in water but the solubility decreases as the molecular mass increases.

(R) Distinction between aldehydes and ketones can be made by Tollens' reagent

❖ **Short Answer Type Questions (2 and 3 marks)**

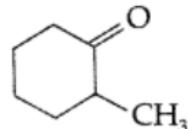
1. Acetaldehyde undergoes a reaction to form a product which exhibits properties of aldehyde and alcohols
 - (i) Name the reaction and give equation.
 - (ii) Write the structural formula of the product formed.
 - (iii) What are the reagents other than acetaldehyde required for the reaction to take place?
2. Write the structural formulae and names of the four possible aldol condensation products from propanal and butanal. In each case indicate which aldehyde acts as nucleophile and which as electrophile.
3. How do you account for the following?
 - (a) Boiling points of aldehydes lie between parent alkanes and corresponding alcohols.
 - (b) Aldehydes and ketones have high dipole moments.
4. Four different bottles containing methyl alcohol, ethyl alcohol, acetic acid and acetone have lost their labels.
What chemical tests would be performed to identify them?
5. Four different bottles containing isopropyl iodide, acetone, propionaldehyde and heptane have lost their labels.
What chemical tests would be performed to identify them?
6. How would you distinguish between:
 - (a) Solutions of acetic acid, formic acid and ethanol?
 - (b) Calcium formate and calcium acetate?
 - (c) Acetic acid and acetone?
7. Arrange the following in order of increasing acidity:
 - (i) Propanoic acid, chloro ethanoic acid, 3-bromopropanoic acid and trichloroacetic acid.
 - (ii) 2-Fluorobutanoic acid, 2-iodobutanoic acid, 2-bromobutanoic acid and butanoic acid.
 - (iii) Acetic acid, 2-methyl propanoic acid, 2,2-dimethyl propanoic acid.
8. How do you account for the following?
 - (a) NaHSO_3 is used for the purification of aldehydes and ketones.
 - (b) Iodoform is obtained by the reaction of acetone with hypoiodite but not with iodide
9. Do the following conversions.
(a)Methyl chloride to acetone. (b) Propan-1-ol to propanoic acid.

10. (a) Write the structure of the product formed in the following reaction .



(b) Give the structure and IUPAC name of the product formed when propanone is reacted with methylmagnesium bromide followed by hydrolysis.

(c) Write the IUPAC name of the following

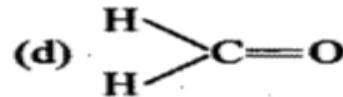
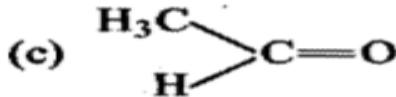
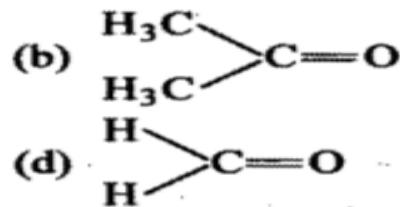
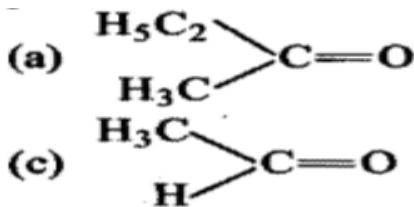


CASE BASED QUESTIONS

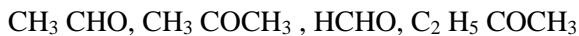
Q.I Aldehyde and ketones are specially susceptible to nucleophilic addition reaction because carbonyl is polar. Positive charge on carbon makes it reactive towards. This addition is catalyzed by acid. Reactivity of carbonyl towards nucleophilic addition increases with increase in the electron deficiency at carbonyl carbon. Thus (-I.E.) group increase while (+I.E.) groups decrease the reactivity of carbonyl compounds.

Answer the following question

- 1.Which is most reactive to give nucleophilic addition - FCH₂CHO and CICH₂CHO?
2. Which among the following carbonyl compounds is most polar

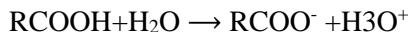


3. Arrange the following in order of their increasing reactivity towards HCN :-

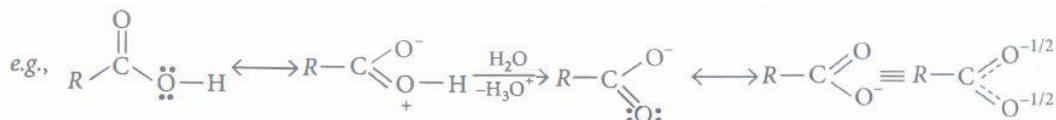


4. Mention the criteria for aldehyde to undergo aldol condensation?

Q.II Carboxylic acids dissociate in water to give carboxylate ion and hydronium ion.



The acidity of carboxyl group is due to the presence of positive charge on oxygen which liberates proton. The carboxylate ion formed is resonance stabilised.



Carboxylic acids are stronger acids than phenols. Electron withdrawing groups (EWG) increase the acidity of

carboxylic acids by stabilising the conjugate base through delocalisation of negative charge by inductive and/ or resonance effects. Electron donating group (EDG) decrease the acidity by destabilising the conjugate base.

Answer the following questions:

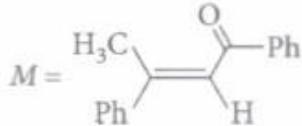
1. Complete the reaction



2. Write one chemical reactions showing the acidic property of carboxylic acid?

3. Arrange the following in decreasing order of their acidic strength and give the reason for your answer. $\text{CH}_3\text{CH}_2\text{OH}$, CH_3COOH , CICH_2COOH , FCH_2COOH , $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$.

4. A tertiary alcohol H upon acid catalysed dehydration gives a product I. Ozonolysis of I leads to compounds J and K. Compound J upon reaction with KOH gives benzyl alcohol and a compound L, whereas K on reaction with KOH gives only M. The structures of compound J, K and L, respectively, are-



5 MARKS QUESTIONS

1. How will you differentiate between?

- (i) Acetaldehyde and acetone.
- (ii) Aldehydes and ketones with - (a) Tollens' reagent (b) Fehling's solution.
- (iii) Acetone and diethyl ether.
- (iv) Formaldehyde and acetaldehyde.
- (v) Formaldehyde and ethyl alcohol.

2. What happens when?

- (i) Formic acid is heated with conc. H_2SO_4
- (ii) Dry chlorine is passed through acetic acid in presence of sunlight.
- (iii) Oxalic acid is heated with glycerol.
- (iv) Formic acid is reacted with ammoniacal silver nitrate solution.
- (v) Acetic acid is heated with phosphorus pentoxide.

3. Answer the following:

- (i) Why 100% pure acetic acid is named glacial acetic acid?
- (ii) Carboxylic acids with five or fewer carbon atoms are water soluble but, higher ones are insoluble
- (iii) Why the bond length of C=O in carboxylic acids is a bit longer than in aldehydes?
- (iv) Highly branched carboxylic acids are less acidic than unbranched acids.
- (v) Acetic acid can be halogenated in presence of phosphorus and chlorine but formic acid cannot be halogenated in the same way.

MCQ(1 mark each)

Ans. 1 b 2 c 3 b 4 b 5 a
 6 d 7 b 8 b 9 c 10 b 11 d 12 d 13 b 14 d
 15 d

ASSERTION REASON TYPE QUESTIONS(1 mark each)

1. (a) 2. (d) 3. (C) 4.(a) 5. (d)
 6.(a) 7. (a) 8.(e) 9.(d) 10. (b)

SHORT ANSWER TYPE QUESTIONS(2 MARKS / 3 MARKS)

- 1 (i) **Aldol condensation**
 $\text{CH}_3\text{CHO} + \text{HCH}_2\text{CHO} \xrightarrow{\text{H}} \text{CH}_3\text{CH(OH)}\text{CH}_2\text{CHO}$
- (ii) Structure $\begin{array}{c} \text{CH}_3 \\ | \\ \text{C} \\ | \\ \text{OH} \\ | \\ \text{CH}_2-\text{CHO} \end{array}$
- (iii) Other reagent required is dilute NaOH or mild alkali.

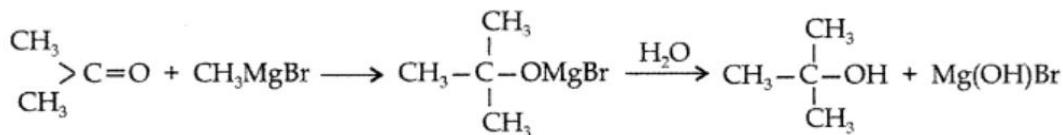
- 2 (i) $\text{CH}_3\text{CH}_2\text{CHO} + \text{HHC}-\overset{\text{CH}_3}{\text{CHO}} \xrightarrow{\text{OH}^-} \begin{array}{ccccccc} & & & & & & \\ & \overset{5}{\text{CH}_3} & \overset{4}{\text{CH}_2} & \overset{3}{\text{CH}} & \overset{2}{\text{CH}} & \overset{1}{\text{CHO}} & \\ & | & | & | & | & | & \\ & \text{OH} & \text{CH}_3 & \text{OH} & \text{CH}_3 & & \end{array}$
 Propanal acts both as electrophile as well as nucleophile.
 3-Hydroxy -2-methylpentanal
- (ii) $\text{CH}_3\text{CH}_2\text{CHO} + \text{HHC}-\overset{\text{CH}_2\text{CH}_3}{\text{CHO}} \xrightarrow{\text{OH}^-} \begin{array}{ccccccc} & & & & & & \\ & \overset{5}{\text{CH}_3} & \overset{4}{\text{CH}_2} & \overset{3}{\text{CH}} & \overset{2}{\text{CH}} & \overset{1}{\text{CHO}} & \\ & | & | & | & | & | & \\ & \text{OH} & \text{CH}_2\text{CH}_3 & \text{OH} & & & \end{array}$
 Propanal as electrophile and butanal as nucleophile.
 2-Ethyl -3-hydroxypentanal
- (iii) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} + \text{HHC}-\overset{\text{CH}_3}{\text{CHO}} \xrightarrow{\text{OH}^-} \begin{array}{ccccccc} & & & & & & \\ & \overset{6}{\text{CH}_3} & \overset{5}{\text{CH}_2} & \overset{4}{\text{CH}_2} & \overset{3}{\text{CH}} & \overset{2}{\text{CH}} & \overset{1}{\text{CHO}} \\ & | & | & | & | & | & \\ & \text{OH} & \text{CH}_3 & \text{OH} & \text{CH}_3 & & \end{array}$
 Butanal as electrophile and propanal as nucleophile.
 3-Hydroxy -2-methylhexanal
- (iv) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} + \text{HHC}-\overset{\text{CH}_2\text{CH}_3}{\text{CHO}} \xrightarrow{\text{OH}^-} \begin{array}{ccccccc} & & & & & & \\ & \overset{6}{\text{CH}_3} & \overset{5}{\text{CH}_2} & \overset{4}{\text{CH}_2} & \overset{3}{\text{CH}} & \overset{2}{\text{CH}} & \overset{1}{\text{CHO}} \\ & | & | & | & | & | & \\ & \text{OH} & \text{CH}_2\text{CH}_3 & \text{OH} & \text{CH}_2\text{CH}_3 & & \end{array}$
 Butanal acts both as electrophile as well as nucleophile.
 2-Ethyl -3-hydroxyhexanal

- 3 (a) Alkanes have low boiling points as no hydrogen bonding and no dipole-dipole attractive forces are present. Alcohols have high boiling points as intermolecular hydrogen bonding is present. In aldehydes, dipole-dipole forces are present due to polar nature of carbonyl group. Thus, boiling points of aldehydes lie between alkanes and alcohols.
 (b) The large dipole moment is due to the large contribution" of the polar structure (resonance) to the hybrid.



- 4 (i) Add NaHCO_3 the one which evolves brisk effervescences contains acetic acid.
 (ii) Add NaHSO_3 . The one which forms a white crystalline precipitate contains acetone.
 (iii) Perform iodoform test in remaining two bottles. The one which forms a yellow product with I_2 and NaOH contains ethyl alcohol

(b) IUPAC name : 2-methylpropan-2-ol



(c) IUPAC name : 2-methylcyclohexanone

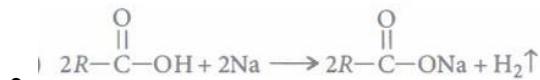
CASE BASED QUESTIONS

QI 1. FCH_2CHO 2. (d)

3. $\text{C}_2\text{H}_5\text{COCH}_3 < \text{CH}_3\text{COCH}_3 < \text{CH}_3\text{CHO} < \text{HCHO}$

4. Aldehydes which contain α -hydrogen.

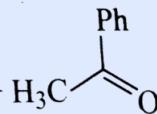
QII 1. $\text{RCOOR}' + \text{H}_2\text{O}$



2.

3. $\text{FCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{C}_6\text{H}_5\text{CH}_2\text{COOH} > \text{CH}_3\text{COOH} > \text{CH}_3\text{CH}_2\text{OH}$

4. Reaction of (J) with KOH suggests that it is Cannizzaro reaction. Therefore, (L) is PhCOOK and (J) is (PhCHO). Structure of (M) is given, and it is α - β -unsaturated ketone. It suggests



that(M) is obtained by the Aldol condensation of (K)

1 i) Ans. Acetaldehyde responds to following tests while acetone does not give any of them:

(a) Acetaldehyde + Schiff's reagent solution \longrightarrow Pink colour

(b) Acetaldehyde + Tollens' reagent \longrightarrow Silver mirror.

(c) Acetaldehyde + Fehling's solution \longrightarrow Red precipitate.

(d) Acetaldehyde + Sodium hydroxide (conc.) \longrightarrow Brown resinous mass

ii) (a) aldehyde + Tollens' reagent \longrightarrow Silver mirror.

(b) aldehyde + Fehling's solution \longrightarrow Red precipitate.

iii) Ans. Acetone forms yellow coloured iodoform when heated with 12 and NaOH, i.e., it gives iodoform test. Diethyl ether does not give this test.

iv) Ans. Acetaldehyde forms yellow precipitate of iodoform with an alkaline solution of iodine, i.e., gives iodoform test. Formaldehyde does not give this test.

v) Ans. Formaldehyde responds to following tests while ethyl alcohol does not give any of them

(a) HCHO + Schiff's reagent Pink colour

(b) HCHO + Tollens' reagent Silver mirror

(c) HCHO + Fehling's solution Red precipitate

Ethyl alcohol gives iodoform test while HCHO does not.

2.	<p>(i) $\text{HCOOH} \xrightarrow{\text{H}_2\text{SO}_4(\text{conc.})} \text{CO} + \text{H}_2\text{O}$</p> <p>(ii) $\text{CH}_3\text{COOH} \xrightarrow[\text{Sunlight}]{\text{Cl}_2} \text{CH}_2\text{ClCOOH}$</p> <p>(iii) At 110°C, formic acid is formed. At 230°C, allyl alcohol is formed.</p> <p>(iv) $\text{HCOOH} + \text{Ag}(\text{NH}_3)_2\text{NO}_3 \longrightarrow \text{Ag} + 2\text{NH}_4\text{NO}_3 + \text{CO}_2$</p> <p>(v) $2\text{CH}_3\text{COOH} \xrightarrow{\text{P}_2\text{O}_5} (\text{CH}_3\text{CO})_2\text{O} + \text{H}_2\text{O}$</p>
3.	<p>(i) The melting point of pure anhydrous acetic acid is 17°C. It is solid below this temperature and looks like 'icy' i.e., glacial</p> <p>(ii) The solubility of RCOOH in water is due to hydrogen bonding of -COOH group and water. R-portion being lyophobic resists solubility. As R gets large, this factor prevails over the first factor and thus, higher acids become insoluble.</p> <p>(iii) Due to resonance, there is considerable contribution of the resonance form, there is some single bond character in C=O bond which makes it somewhat longer than in aldehydes.</p> <p>(iv) The -COOH group of the branched acid is shielded from solvent molecules and cannot be stabilized by solvation as effectively as unbranched acid like the acetate anion.</p> <p>(v) This is HVZ reaction. It occurs only in those carboxylic acids which have α-hydrogen atoms. Acetic acid possesses three α-hydrogen atoms but formic acid does not have even a single α-hydrogen atom. Thus, formic acid does not undergo this reaction</p>