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Introduction (Aldehydes & Ketones) Aldehydes and ketones contain a carbonyl

group.

An aldehyde contains at least one H atom bonded to the carbonyl carbon, whereas the ketone has two alkyl or aryl groups bonded to it.



Introduction (Aldehydes & Ketones)

Aldehyde
$$R = C + C + R'$$

R = H, alkyl or aryl
R and R ' = alkyl or aryl



Introduction (Carboxylic Acids)

The carbonyl compounds in which carbonyl group is bonded to oxygen are known as carboxylic acids, and their derivatives (e.g. esters, anhydrides) while in compounds where carbon is attached to nitrogen and to halogens are called amides and acyl halides respectively.



Aromatic Aldehydes in plants



Nomenclature

The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending -e with -al and -one respectively. In case of aldehydes the longest carbon chain is numbered starting from the carbon of the aldehyde group while in case of ketones the

numbering begins from the end nearer to the carbonyl group.

Nomenclature (contd)

- When the aldehyde group is attached to a ring, the suffix carbaldehyde is added after the full name of the cycloalkane.
- The numbering of the ring carbon atoms start from the carbon atom attached to the aldehyde group.



Nomenclature (contd)



Common & IUPAC names of some aldehydes & ketones

Structure	Common name	IUPAC name	
Aldehydes			
HCHO	Formaldehyde	Methanal	
(CH)-CHCHO	Isobuturaldebyde	Ethanai	
	isobutyraidenyde	2-methylpropanai	
П ₃ С СНО	γ-Methylcyclohexane	3-Methylcyclohexanecarbaldehyde	
CH ₃ CH(OCH ₃)CHO	α-Methoxypropionaldehyde	2-Methoxypropanal	
CH ₃ CH ₂ CH ₂ CH ₂ CHO	Valeraldehyde	Pentanal	
CH ₂ =CHCHO	Acrolein	Prop-2-enal	
СНО	Phthaldehyde	Benzene-1,2-dicarbaldehyde	
CHO Br	m-Bromobenzaldehyde	3-Bromobenzenecarbaldehyde or 3-Bromobenzaldehyde	
<i>Ketones</i> CH ₃ COCH ₂ CH ₂ CH ₃ (CH ₃) ₂ CHCOCH(CH ₃) ₂	Methyl <i>n</i> -propyl ketone Diisopropyl ketone	Pentan-2-one 2,4-Dimethylpentan-3-one	
CCC ^O CH ₃	α-Methylcyclohexanone	2-Methylcyclohexanone	
(CH ₃) ₂ C=CHCOCH ₃	Mesityl oxide	4-Methylpent-3-en-2-one	

Structure of carbonyl group



The carbonyl carbon atom is sp^2 -hybridised 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 an oxygen.

In addition, the oxygen atom also has two non bonding 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.

Structure of carbonyl group (contd)

The carbon-oxygen double bond is polarised due to higher electronegativity of oxygen relative to carbon. Hence, the carbonyl carbon is an electrophilic (Lewis acid), and carbonyl oxygen, a nucleophilic (Lewis base) centre.



Preparation of aldehydes & ketones

By oxidation of alcohol



Preparation of aldehydes & ketones

By dehydrogenation of alcohols



From hydrocarbons

(1) By ozonolysis of alkenes:



Preparation of aldehydes & ketones

From hydrocarbons (contd)

(2) By hydration of alkynes:



Addition of water to ethyne gives acetaldehyde.

All other alkynes give ketones.

Preparation of aldehydes only

From acyl chloride (acid chloride)

Rosenmund reduction



Preparation of aldehydes only From nitriles and esters

Nitriles are reduced to corresponding imine with stannous chloride in the presence of hydrochloric acid, which on hydrolysis give corresponding aldehyde.

 $RCN + SnCl_2 + HCl \longrightarrow RCH = NH \xrightarrow{H_3O} RCHO$

This reaction is called Stephen reaction.

Preparation of aldehydes only (contd)

Nitriles are selectively reduced by diisobutylaluminium hydride, (DIBAL-H) to imines followed by hydrolysis to aldehydes:

$$RCN \xrightarrow{1. \text{AlH(i-Bu)}_2} R-CHO$$

$$CH_3 - CH=CH-CH_2CH_2-CN \xrightarrow{1. \text{AlH(i-Bu)}_2} CH_3 - CH=CH-CH_2CH_2-CHO$$
Esters are also reduced to aldehydes with DIBAL-H.

Preparation of aromatic aldehydes

- From hydrocarbons
- By oxidation of methylbenzene
- Strong oxidising agents oxidise toluene and its derivatives to benzoic acids.
- It is possible to stop the oxidation at the aldehyde stage with suitable reagents

(a) Use of chromyl chloride (CrO₂Cl₂) (Etard reaction) :



Preparation of aromatic aldehydes (contd) Use of chromic oxide (CrO₃): **(b)** CH_{3} CH(OCOCH₃)₂ сно + CrO₃ + (CH₃CO)₂O <u>273-283K</u>→ H₃O⁺ **Benzylidene diacetate** Benzaldehvde side chain chlorination By CH. сно CHCL Cl₂/hv H₂O Toluene Benzaldehvde Benzal chloride **Gatterman - Koch reaction** Bv CO, HCl Anhyd. AlCl,/CuCl Benzaldehyde Benzene

Preparation of ketones only

From acyl chlorides

 $2 R - Mg - X + CdCl_2 \longrightarrow R_2Cd + 2Mg(X)Cl$

From nitriles

$$CH_{3} - CH_{2} - C = N + C_{6}H_{5}MgBr \xrightarrow{ether} CH_{3}CH_{2} - C \xrightarrow{NMgBr} \xrightarrow{H_{3}O^{+}} C_{2}H_{5} - C \xrightarrow{O} C_{6}H_{5}$$
Propiophenone
(1-Phenylpropanone)

Preparation of ketones only (contd)

From benzene or substituted benzenes (Friedel-Crafts acylation reaction)

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Physical properties of aldehydes & ketones

Boiling point

- The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses.
- It is due to weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions.
- Also, their boiling points are lower than those of alcohols of similar molecular masses due to
- absence of intermolecular hydrogen bonding.

Physical properties of aldehydes & ketones

Solubility

The lower members of aldehydes and ketones such as methanal, ethanal and propanone are miscible with water in all proportions, because they form hydrogen bond with water.



However, the solubility of aldehydes and ketones decreases rapidly on increasing the length of alkyl chain.

Chemical Reactions of aldehydes & ketones



Nucleophilic addition reactions

Chemical Reactions of aldehydes & ketones

Reactivity

Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons.

Sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent.

Electronically, aldehydes are more reactive than ketones because two alkyl groups reduce the electrophilicity of the carbonyl more effectively than in aldehydes.

Examples of nucleophilic addition and nucleophilic addition-elimination reactions

(a) Addition of hydrogen cyanide (HCN):



Examples of nucleophilic addition and nucleophilic addition-elimination reactions (contd)

(b) Addition of sodium hydrogensulphite:



The hydrogensulphite addition compound is water soluble and can be converted back to the original carbonyl compound by treating it with dilute mineral acid or alkali.

Therefore, these are useful for separation and purification of aldehydes.

Examples of nucleophilic addition and nucleophilic addition-elimination reactions (contd)

(c) Addition of Grignard reagents:

 $HCHO + RMgX \rightarrow RCH_2OMgX \xrightarrow{H_2O} RCH_2OH + Mg(OH)X$



(d) Addition of alcohols:



Acetals and ketals are hydrolysed with aqueous mineral acids to yield corresponding aldehydes and ketones respectively.

Examples of nucleophilic addition and nucleophilic addition-elimination reactions

H*

(e) Addition of ammonia and its derivatives:

$$\searrow C = 0 + H_2 N - Z \iff \left[\swarrow OH \right] \longrightarrow C = N - Z + H_2 O$$

 $Z = Alkyl, aryl, OH, NH_2, C_6H_5NH, NHCONH_2,$

Examples of nucleophilic addition and nucleophilic addition - elimination reactions (contd)

(e) Addition of ammonia and its derivatives: (contd)

z	Reagent name	Carbonyl derivative	Product name
-H	Ammonia	C=NH	Imine
-R	Amine	C=NR	Substituted imine (Schiff's base)
—ОН	Hydroxylamine	C=N-OH	Oxime
$-NH_2$	Hydrazine		Hydrazone
	Phenylhydrazine	C=N-NH	Phenylhydrazone
	2,4-Dinitrophenyl- hydrazine		2,4 Dinitrophenyl- hydrazone
O II —NH—C—NH ₂	Semicarbazide	$\sum_{C=N-NH}^{O} - C - NH^{2}$	Semicarbazone

Reduction of aldehydes and ketones

(i) Reduction to alcohols:

Reduction of aldehyde and ketones

(ii) Reduction to hydrocarbons :

Clemmensen reduction



Wolff-Kishner reduction



Oxidation of aldehydes and ketones

Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate, etc. Even mild oxidising agents, mainly Tollens' reagent and Fehlings' reagent also oxidise aldehydes.

$R-CHO \longrightarrow R-COOH$

Ketones are generally oxidised under vigorous conditions, i.e., strong oxidising agents and at elevated temperatures.

$$R \xrightarrow{1}{} CH_{2} \xrightarrow{2}{} CH_{2} \xrightarrow{R'} \xrightarrow{[O]} R \xrightarrow{-COOH} + R' - CH_{2} \xrightarrow{-COOH} (By cleavage of C_{1} - C_{2} bond) + R \xrightarrow{-COOH} + R' - COOH (By cleavage of C_{2} - C_{3} bond)$$

The mild oxidising agents are used to distinguish aldehydes from ketones

(i) Tollens' test:

$RCHO + 2[Ag(NH_3)_2]^* + 3 \overline{O}H \longrightarrow RCO\overline{O} + 2Ag + 2H_2O + 4NH_3$

(ii) Fehling's test:

Fehling reagent comprises of two solutions, Fehling solution A and Fehling solution B. Fehling solution A is aqueous copper sulphate and Fehling solution B is alkaline sodium potassium tartarate (Rochelle salt).

$$R-CHO + 2Cu^{2+} + 5\overline{O}H \longrightarrow RCO\overline{O} + Cu_2O + 3H_2O$$

Red-brown ppt

Aromatic aldehydes do not respond to this test.
The mild oxidising agents are used to distinguish aldehydes from ketones

(iii) Oxidation of methyl ketones by haloform reaction :

Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom (methyl ketones) are oxidised by sodium hypohalite to sodium salts of corresponding carboxylic acids having one carbon atom less than that of carbonyl compound. The methyl group is <u>converted to haloform</u>.



lodoform reaction with sodium hypoiodite is also used for detection of CH_3CO group or $CH_3CH(OH)$ group which produces CH_3CO group on oxidation.

Acidity of α -hydrogens of aldehydes and ketones:

The acidity of α -hydrogen atoms of carbonyl compounds is due to the strong electron withdrawing effect of the carbonyl group and resonance stabilisation of the conjugate base.

(i) Aldol condensation:

Aldehydes and ketones having atleast one α -hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form β -hydroxy aldehydes (aldol) or β -hydroxy ketones (ketol), respectively. This is known as Aldol reaction.



The aldol and ketol readily lose water to give α , β -unsaturated carbonyl compounds which are aldol condensation products and the reaction is called Aldol condensation.

(ii) Cross aldol condensation:

When aldol condensation is carried out between two different aldehydes and / or ketones, it is called cross aldol condensation. If both of them contain α -hydrogen atoms, it gives a mixture of four products.



(ii) Cross aldol condensation: (contd)

Ketones can also be used as one component in the cross aldol reactions.

$$\begin{array}{c} & & & \\ & &$$

Other reactions

(i) Cannizzaro reaction:

Aldehydes which do not have an α -hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali. In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt.



Other reactions

(ii) Electrophilic substitution reaction:

Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and metadirecting group.



Uses of aldehydes & ketones

Formaldehyde is well known as formalin (40%) solution used to preserve biological specimens and to prepare bakelite (a phenol-formaldehyderesin), urea-formaldehyde glues and other polymeric products.

Benzaldehyde is used in perfumery and in dye industries. Acetone and ethyl methyl ketone are common industrial solvents.

Carboxylic Acids

Carbon compounds containing a carboxyl functional group, -COOH are called carboxylic acids.

The carboxyl group, consists of a carbonyl group attached to a hydroxyl group, hence its name carboxyl.

Carboxylic acids may be aliphatic (RCOOH) or aromatic (ArCOOH) depending on the group, alkyl or aryl, attached to carboxylic carbon.

Some higher members of aliphatic carboxylic acids $(C_{12} - C_{18})$ known as fatty acids, occur in natural fats as esters of glycerol.

Nomenclature of Carboxylic Acids

In the IUPAC system, aliphatic carboxylic acids are named by replacing the ending -e in the name of the corresponding alkane with - oic acid.

In numbering the carbon chain, the carboxylic carbon is numbered one.

For naming compounds containing more than one carboxyl group, the ending -e of the alkane is retained.

Nomenclature of Carboxyl Group (contd)

Structure	Common name	IUPAC name
нсоон	Formic acid	Methanoic acid
CH ₃ COOH	Acetic acid	Ethanoic acid
CH ₃ CH ₂ COOH	Propionic acid	Propanoic acid
CH ₃ CH ₂ CH ₂ COOH	Butyric acid	Butanoic acid
(CH ₃) ₂ CHCOOH	Isobutyric acid	2-Methylpropanoic acid
HOOC-COOH	Oxalic acid	Ethanedioic acid
HOOC -CH ₂ -COOH	Malonic acid	Propanedioic acid
HOOC -(CH ₂) ₂ -COOH	Succinic acid	Butanedioic acid
HOOC -(CH ₂) ₃ -COOH	Glutaric acid	Pentanedioic acid
HOOC -(CH ₂) ₄ -COOH	Adipic acid	Hexanedioic acid
HOOC -CH ₂ -CH(COOH)-CH ₂ -COOH	_	Propane-1, 2, 3- tricarboxylic acid







Benzoic acid

Phenylacetic acid

Phthalic acid

Benzenecarboxylic acid (Benzoic acid)

2-Phenylethanoic acid

Benzene-1, 2-dicarboxylic acid

Structure of Carboxyl Group

- In carboxylic acids, the bonds to the carboxyl carbon lie in one plane and are separated by about 120°.
- The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure.



Preparation of Carboxylic Acids

1. From primary alcohols and aldehydes $RCH_2OH \xrightarrow{1. alkaline KMnO_4} RCOOH$ $2. H_3O$ $RCH_2OH \xrightarrow{1. alkaline KMnO_4} RCOOH$ $2. H_3O$ $CH_3(CH_2)_8CH_2OH \xrightarrow{CrO_3-H_2SO_4} CH_3(CH_2)_8COOH$ 1-DecanolDecanoic acid

2. From alkylbenzenes

Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid or acidic or alkaline potassium permanganate.

The entire side chain is oxidised to the carboxyl group irrespective of length of the side chain. Primary and secondary alkyl groups are oxidised in this manner while

tertiary group is not affected.



3. From nitriles and amides



4. From Grignard reagents

R-Mg-X + O=C=O
$$\xrightarrow{\text{Dry ether}} R - C \xrightarrow{0} \xrightarrow{\text{H}_{3}O^{+}} RCOOH$$

Useful for converting alkyl halides into corresponding carboxylic acids having one carbon atom more than that present in alkyl halides (ascending the series).

5. From acyl halides and anhydrides



Preparation of Carboxylic Acids (contd)

6. From esters



Physical Properties of carboxylic acids

Boiling Point

Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acid molecules through intermolecular

hydrogen bonding.



Physical Properties of carboxylic acid

Solubility

Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water. The solubility decreases with increasing number of carbon atoms. Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part.



Chemical reactions of carboxylic acid **Reactions** Involving Cleavage of O-H Bond Acidity Reactions with metals and alkalies $2R-COOH + 2Na \longrightarrow 2R-COONa^{+}$ + Н, Sodium carboxylate $R-COOH + NaOH \longrightarrow R-COONa^+ +$ H₀ $R-COOH + NaHCO_3 \longrightarrow R-COONa^+ + H_2O + CO_2$ This reaction is used to detect the presence of carboxyl group in an organic compound.

Chemical reactions of carboxylic acid

Reactions Involving Cleavage of O-H Bond (Contd) Carboxylic acids dissociate in water to give resonance stabilised carboxylate anions and hydronium ion.



where K_{eq} , is equilibrium constant and K_a is the acid dissociation constant.

For convenience, the strength of an acid is generally indicated by its pK_a value rather than its K_a value.

 $pK_a = -\log K_a$

Smaller the pK_a , the stronger the acid (the better it is as a proton donor). Strong acids have pK_a values < 1, the acids with pK_a values between 1 and 5 are considered to be moderately strong acids, weak acids have pK_a values between 5 and 15, and extremely weak acids have pK_a values > 15.

Carboxylic acids are weaker than mineral acids, but they are stronger acids than alcohols and phenols. The higher acidity of carboxylic acids as compared to phenols is due to the following reason.

The conjugate base of carboxylic acid, a carboxylate ion, is stabilised by two equivalent resonance structures in which the negative charge is at the more electronegative oxygen atom.

The conjugate base of phenol, a phenoxide ion, has non-equivalent resonance structures in which the negative charge is at the less electronegative carbon atom.

The negative charge is delocalised over two electronegative oxygen atoms in carboxylate ion whereas it is less effectively delocalised over one oxygen atom and less electronegative carbon atoms in phenoxide ion

Thus, the carboxylate ion is more stabilised than phenoxide ion, so carboxylic acids are more acidic than phenols.

Effect of substituents on the acidity of carboxylic acids

Electron withdrawing groups increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of the negative charge by inductive and/or resonance effects. Conversely, electron donating groups decrease the acidity by destabilising the conjugate base.



Electron withdrawing group (EWG) stabilises the carboxylate anion and strengthens the acid



Electron donating group (EDG) destabilises the carboxylate anion and weakens the acid

Effect of substituents on the acidity of carboxylic acids

The effect of the following groups in increasing acidity order is

$Ph < I < Br < Cl < F < CN < NO_2 < CF_3$

Thus, the following acids are arranged in order of decreasing acidity (based on pKa values):

 $CF_3COOH > CCI_3COOH > CHCI_2COOH > NO_2CH_2COOH > NC-CH_2COOH >$

$$\label{eq:FCH2} \begin{split} \mathsf{FCH}_2\mathsf{COOH} > \mathsf{CICH}_2\mathsf{COOH} > \mathsf{BrCH}_2\mathsf{COOH} > \mathsf{HCOOH} > \ \mathsf{CICH}_2\mathsf{CH}_2\mathsf{COOH} > \\ & (\mathsf{continue}) \end{split}$$

 $C_6H_5COOH > C_6H_5CH_2COOH > CH_3COOH > CH_3CH_2COOH$ (continue)

Effect of substituents on the acidity of carboxylic acids

Direct attachment of groups such as phenyl or vinyl to the carboxylic acid, increases the acidity of corresponding carboxylic acid, contrary to the decrease expected due to resonance effect.



This is because of greater electronegativity of sp² hybridised carbon to which carboxyl carbon is attached.



The presence of electron withdrawing group on the phenyl of aromatic carboxylic acid increases their acidity while electron donating groups decrease their acidity.

Reactions involving Cleavage of C-OH bond

1. Formation of anhydride



2. Esterification

RCOOH + R'OH
$$\stackrel{H^+}{=}$$
 RCOOR' + H₂O

Mechanism of esterification of carboxylic acids:



Reactions involving Cleavage of C-OH bond (contd)

3. Reactions with PCI₅, PCI₃ and SOCI₂

- $RCOOH + PCl_5 \longrightarrow RCOC1 + POCl_3 + HCl_5$
- $3R_{COOH} + PCl_3 \longrightarrow 3R_{COC1} + H_3PO_3$
- $RCOOH + SOCl_2 \longrightarrow RCOC1 + SO_2 + HC1$

Reactions involving Cleavage of C-OH bond (contd)

4. Reaction with ammonia



Reactions Involving –COOH Group

1. Reduction



Sodium borohydride does not reduce the carboxyl group.

Reactions Involving –COOH Group (contd)

2. Decarboxylation

NaOH & CaO → R-H + Na₂CO₃ Heat

Kolbe electrolysis

R-COONa

Alkali metal salts of carboxylic acids also undergo decarboxylation on electrolysis of their aqueous solutions and form hydrocarbons having twice the number of carbon atoms present in the alkyl group of the acid. The reaction is known as Kolbe electrolysis.

Substitution Reactions in the Hydrocarbon Part

1. Halogenation (Hell-Volhard-Zelinsky reaction)

Carboxylic acids having an α -hydrogen are halogenated at the α -position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α -halocarboxylic acids. The reaction is known as Hell-Volhard-Zelinsky reaction.

$$\begin{array}{c} \text{R-CH}_2\text{-COOH} & \xrightarrow{(i) X_2/\text{Red phosphorus}} & \text{R-CH-COOH} \\ \hline (ii) H_2\text{O} & & \downarrow \\ & X \\ & X \\ & X \\ & X = \text{Cl, Br} \\ & \alpha - \text{Halocarboxylic acide} \end{array}$$

Substitution Reactions in the Hydrocarbon Part

2. Ring substitution

Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl group acts as a deactivating and meta-directing group.



They do not undergo Friedel-Crafts Reaction because carboxyl group is deactivating and the catalyst AICl₃ (Lewis acid) gets bonded to the carboxyl group.

Uses of Carboxylic Acids

- Methanoic acid is used in rubber, textile, dyeing, leather and electroplating industries.
- Ethanoic acid is used as solvent and as vinegar in food industry.
- Hexanedioic acid is used in the manufacture of nylon-6, 6. Esters of benzoic acid are used in perfumery.
- Sodium benzoate is used as a food preservative.

Higher fatty acids are used for the manufacture of soaps and detergents.

