

# CONCEPT MAP

# ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Being important constituents of fabrics, flavourings, plastics and drugs, carbonyl compounds are of utmost importance to organic chemistry while carboxylic acids are amongst the earliest organic compounds to be isolated from nature and are still known by their common names.

## Structure and Nomenclature

### Aldehydes

- $R-\overset{\text{O}}{\parallel}{C}-H$  where,  $R = H$ , alkyl or aryl group.
- In IUPAC system, aldehydes are named as *alkanals*.

### Ketones

- $R-\overset{\text{O}}{\parallel}{C}-R'$  where  $R$  and  $R'$  both can be same or different groups.
- In IUPAC system, they are named as *alkanones*.

## ALDEHYDES AND KETONES

## Physical Properties

- Solubility in water  $\propto \frac{1}{\text{Molecular mass}}$
- Compounds having upto four carbon atoms are soluble in water due to hydrogen bonding.
- Due to dipole-dipole interactions their b.p.s. are higher than the corresponding hydrocarbons or ethers but lesser than alcohols or carboxylic acids which have intermolecular H-bonding.
- Due to two electron donating alkyl groups, ketones have higher b.p.s. than the corresponding aldehydes.

## Distinction Tests

Test	Aldehydes	Ketones
Schiff's reagent	Pink colour	No colour
Fehling's solution	Red ppt.	No ppt.
Tollens' reagent	Silver mirror	No ppt.
Sodium hydroxide	Brown resinous mass (except HCHO)	No reaction
Alkaline sodium nitroprusside	A deep red colour (except HCHO)	Red colour which changes to orange

## Structure and Nomenclature

### Carboxylic acids

- $R-\overset{\text{O}}{\parallel}{C}-OH$  where,  $R = H$ , alkyl or aryl group.
- In IUPAC system, they are named as *alkanoic acids*.

## Physical Properties

- Solubility in water  $\propto \frac{1}{\text{Molecular mass}}$
- High b.pt. due to intermolecular hydrogen bonding.
- M.p.s. and b.p.s. of aromatic acids are usually higher than those of aliphatic acids.

## CARBOXYLIC ACIDS

## Chemical Properties

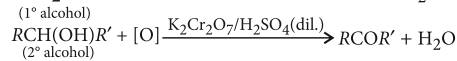
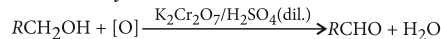
- Acidity order:** Carboxylic acids > Phenols > Alcohols
- EDG decreases the acidity and EWG increases the acidity.
- More the electronegativity of the atom attached to the carboxyl group, more will be the acidity.

## Distinction Tests

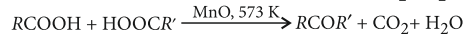
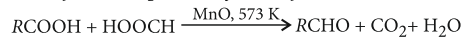
Test	Carboxylic acids	Phenols	Alcohols
$NaHCO_3$	Brisk effervescence of $CO_2$ gas	No reaction	No reaction
$FeCl_3$	Buff coloured ppt.	Violet, blue or red colour	No reaction

## Preparation

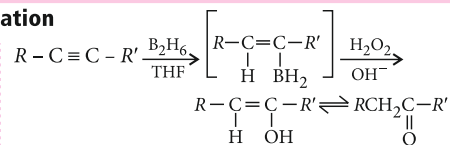
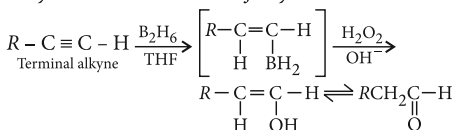
### Oxidation of alcohols:



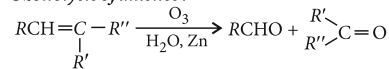
### Catalytic decomposition of carboxylic acids:



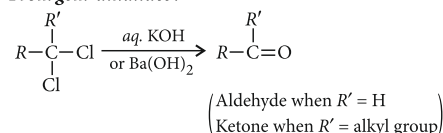
### Hydroboration-oxidation of alkynes:



### Ozonolysis of alkenes:

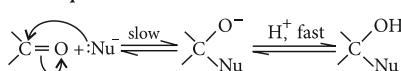


### From gem-dihalides:



## Chemical Properties

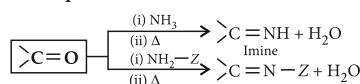
### Nucleophilic addition reactions:



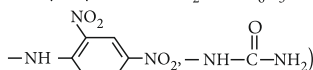
### Reactivity order:

Aldehydes > Ketones (steric and electronic reasons)  
HCHO > RCHO > PhCHO > RCOR > RCOPh > PhCOPh

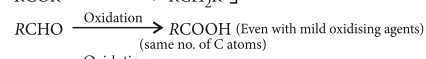
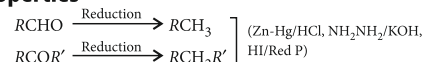
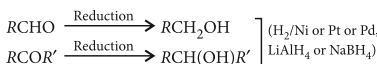
### Nucleophilic addition-elimination reactions:



(Z = alkyl, aryl, -OH, -NH<sub>2</sub>, -NHC<sub>6</sub>H<sub>5</sub>,

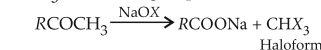


### Reduction and oxidation:

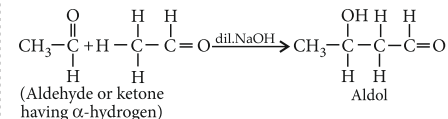


### Haloform reaction:

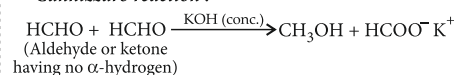
Given by compounds having  $CH_3CO-$  group or  $CH_3CH(OH)-$  group



### Aldol condensation:

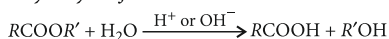


### Cannizzaro reaction:

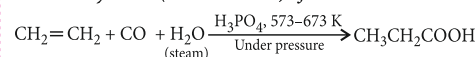


## Preparation

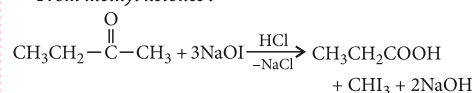
### Hydrolysis of esters:



### Carbonylation (Koch reaction) of alkenes:

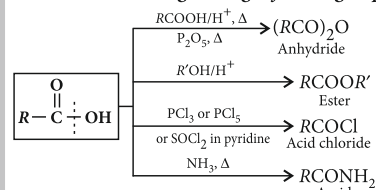


### From methyl ketones:

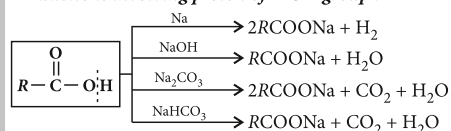


## Chemical Reactions

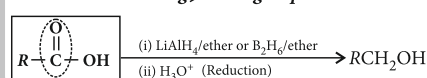
### Reactions involving cleavage of -OH group:



### Reactions involving proton of -OH group:

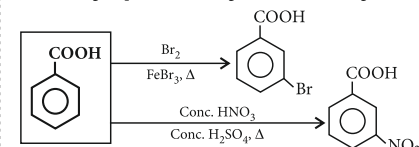


### Reactions involving >C=O group:

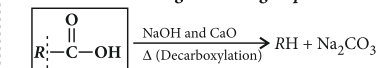


### Ring substitution in aromatic acids:

-COOH group is deactivating and meta directing.



### Reactions involving -COOH group:



### Reactions involving -R group:

