Reduction, Oxidation & Hydrolysis Reactions

Section (A) : Reduction-1

Introduction :

Reduction covers both the addition of hydrogen (or deuterium) to a double bond and the replacement of an atom or group by hydrogen (or deuterium). In other words, reduction means hydrogenation or hydrogenolysis.

Reduction can be carried out in following ways:

- (a) Catalytic hydrogenation
- (c) Metal hydrides reduction
- Metal/proton (acid) reduction Miscellaneous Reductions

1.1 Catalytic hydrogenation :

Hydrogenation using $H_2(g)$ on metal surface or other suitable catalyst is called catalytic hydrogenation. A catalyst provides a new pathway for the reaction that involves lower free energy of activation.

(b)

(d)



Heterogeneous hydrogenation catalysts typically involve finely divided platinum. The catalysts used can be divided into two broad classes, (a) Heterogeneous catalysts (b) Homogeneous catalysts. Both of which mainly consist of transition metals and their compounds :

(i) Heterogeneous catalysts : (catalysts insoluble in the reaction medium) In heterogeneous catalytic hydrogenation catalysts are used in powdered form. Raney nickel (Ni), Palladium on charcol (Pd/C), Platinum metal or its oxide are common heterogeneous catalysts. Facts of catalysis :

(i) Substrate molecules are assumed to undergo homolysis into atoms at the surface of the catalyst.

(ii) The substrate is chemisorbed on the surface of the catalyst and hydrogenation takes place.

(iii) The process is exothermic.

Note : (If H₂ and D₂ mixture is used with a Pt catalyst, the two isotopes quickly scramble to produce a random mixture of HD, H₂ and D₂. (No scrambling occurs in the absence of the catalyst.) The product has both D and H atoms).

Catalytic Reduction of Functional Groups Using H₂/Pd(C) or H₂/Pt or H₂/Ni

 $R-CH=CH-R + H_2 \xrightarrow{\text{Ni or Pd}} R-CH_2-CH_2-R + heat$

| Substrate | Product |
|------------------|------------------------------------|
| RCOCI | RCH ₂ OH |
| RNO ₂ | RNH ₂ |
| RC≡CR | RCH ₂ CH ₂ R |
| RCHO | RCH ₂ OH |
| RCH=CHR | RCH ₂ CH ₂ R |
| RCOR | RCHOHR |
| RCN | RCH ₂ NH ₂ |

- Note: (i) Generally RCOOH, RCOOR, RCONH₂ groups are not reduced by catalytic hydrogenation.
 (ii) Stereochemistry of catalytic hydrogenation: The above reaction is syn addition (addition takes place from the same side of alkene or alkyne).
- (ii) Homogeneous catalysis : (catalysts soluble in the reaction medium). It uses reactants and catalyst in the same phase. Both hydrogen atoms **usually** add from the same side of the molecule. Common example : Use of Wilkinsion catalyst Rh $[(C_6H_5)_3P]_3CI$.

(iii) Lindlar's catalyst : [H₂/Pd, CaCO₃, quinoline]

It is a poisoned palladium catalyst. It is composed of powdered calcium carbonate coated with palladium and poisoned with quinoline. It is used to carry out partial reduction of alkyne to alkene and acid chloride to aldehyde.

Stereochemistry : Syn addition.



Note : Nickel boride Ni₂B **(P-2 catalyst)** (made from Nickel acetate and sodium borohydride) is an excellent alternative catalyst for the conversion of alkyne into alkene. Stereochemistry : Syn addition.

Ni(OCOCH₃)₂ $\xrightarrow{\text{NaBH}_4}$ Ni₂B.

(iv) Rosenmund catalyst : [H₂/Pd, BaSO₄, quinoline] Hydrogenation in presence of H₂/Pd/BaSO₄ is called Rosenmund Reduction. It reduces alkyne to alkene and acid halide to aldehyde. It is poisoned palladium catalyst, composed of powdered barium sulphate coated with palladium, poisoned with quinoline or sulphur.

Stereochemistry : Syn addition.

(a)
$$CH_3-C=C-CH_3 \xrightarrow{H_2,Pd, BaSO_4, S} \xrightarrow{H_3C} C=C \xrightarrow{CH_3} H$$

cis-2-butene
(b) $CH_3-C-CI \xrightarrow{H_2,Pd, BaSO_4, S} CH_3-CHO$

1.2 Metal/proton (acid) reduction :

Reduction by dissolving metals is based on the fact that the metal acts as a source of electrons. **Step-1**: Metals give electrons to the electrophilic species and form anion **Step-2**: Proton is abstracted from the acidic source.

$$A-B \xrightarrow{\overline{e}} A^{\bullet} + \overline{B}; \text{ or } \overline{A}; + B^{\bullet} \xrightarrow{H^{+}} A^{\bullet} + B-H$$
$$A=B \xrightarrow{\overline{e}} : A^{\bullet}-B^{\bullet} \text{ or } A^{\bullet} - B; A^{\bullet}-BH$$

(i) Birch reduction [Na or Li/NH₃(liq.) or (ethyl alcohol)] :

Alkyne and Aromatic Compounds are reduced by Na or Li/NH_3 . Alkynes are reduced to trans alkene. Stereochemistry : anti addition.

$$R-C=C-R \xrightarrow{Na/NH_3} \xrightarrow{R} C = C \xrightarrow{H} (anti addition)$$

Benzene ring is reduced at 1, 4-position.

Typical example of reduction for aromatic system :

Presence of alkyl, alkoxy, amines reduces the benzene ring at ortho position.

(electron releasing group G - R, - OR, - NH_2)



Presence of nitro, cyano, carboxylic, keto or aldehyded group reduces the benzene ring at ipso position.



(ii) Bouvealt-Blanc reduction [Na/C₂H₅OH] :

Reduction of aldehydes, ketones, acidhalides, esters or cyanide by means of excess of Na/C₂H₅OH is called Bouvealt-Blanc reduction.

Na + C_2H_5OH is mild reducing agent.

| Reagent | Na/C₂H₅OH | Na/C₂H₅OH | Na/C₂H₅OH | Na/C₂H₅OH | Na/C₂H₅OH |
|----------|------------|------------|-----------|-----------|-------------|
| Reactant | Aldehyde | Ketone | Cyanide | Ester | acid halide |
| Product | 1° alcohol | 2° alcohol | 1° amine | 1° alchol | 1° alchol |

CH₃CHO $\xrightarrow{Na/C_2H_5OH}$ CH₃CH₂OH Acetaldehyde Ethanol

(iii) Stephen's Reductions : [SnCl₂/HCl]

When reduction of cyanide is carried out with acidified stannous chloride (SnCl₂/HCl) at room temperature, imine hydrochloride is obtained. Which on subsequent hydrolysis with boiling water gives aldehyde. This specific type of reduction of nitrile is called stephen's reduction.

$$R-C=N - (i) SnCl_2 /HCl (ii) H_2O (Partial Reduction) R-CHO (Aldehvde) R-CHO (Aldehvde) R-CHO (Aldehvde) R-CHO (Partial Reduction) R-CHO (Partial$$

(iv) Clemmensen's Reduction : [Zn-Hg/Conc. HCI]

It is used to prepare alkanes from carbonyl compounds (Aldehyde and ketones in absence of acid sensitive groups).

$$C = O \underbrace{Zn - Hg / HCl}_{sp^2} \xrightarrow{Conc.}_{sp^3}$$

Mechanism :



Note: Clemmensen reduction is avoid to use for compounds which have acid sensitive group. [Like: Alcohol, Alkene, Alkyne, Ether].

Section (B): Reduction-2

1.3 Metal hydrides reduction

Certain complex metal and boron hydrides, are important reagents for reduction.

(i) LiAIH₄ (LAH) Lithium aluminium hydride [LiAIH₄/ Ether or THF] :

| LA | LAH is most common and versatile reagent. It is sensitive to protic solvent and therefore used in ether. | | | | | | | | | |
|----------|--|--------------------|----------------------------|----------------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| Reagent | LiAIH ₄ | LiAIH ₄ | LiAIH ₄ /Excess | LiAIH ₄ /Excess | LiAIH ₄ |
| Reactant | Aldehyde | Ketone | Acid | Acidanhydride | Acid chloride | Ester | Cyanide | Amide | Isocyanide | Nitro |
| Product | 1º alcohol | 2º alcohol | 1º alcohol | 1º alcohol | 1º alcohol | 1º alcohol | 1º amine | 1º amine | 2º amine | 1º amine |
| | | | | | | | | | | |

Note : Alkene, alkyne, benzene rings are not reduced by LiAlH₄ in ether but it is reported that

(*) double bond can be reduced by LiAIH₄ / THF in few cases like :

 $Ph-CH=CH-CHO \xrightarrow{(i) LiAIH_4-THF} Ph-CH_2-CH_2-CH_2OH$

[Cinnamaldehyde]

Sodium borohydride [NaBH₄ / C₂H₅OH or Ether] : (ii)

It is more specific than LAH as a reducing agent. It reduces ketones and aldehydes to the corresponding alcohols without affecting other functional groups, reduces acid chlorides to 1º alcohols. It does not reduce any other derivative of acid. It is effective even in protic solvent like alcohol.

| , | | | | | | |
|----------|------------|------------|---------------|--|--|--|
| Reagent | NaBH₄ | NaBH₄ | NaBH₄ | | | |
| Reactant | Aldehyde | Ketone | Acid chloride | | | |
| Product | 1º alcohol | 2º alcohol | 1º alcohol | | | |
| | | | | | | |

(iii) Diisobutyl Aluminium Hydride [DIBAL-H / Inert solvent] :

Diisobutyl aluminium hydride is parallel to LAH (Lithium aluminium hydride) as a reducing agent but it is more selective.

| Reagent | DiBAL-H/(–78⁰C) | DiBAL-H | | | |
|---|-----------------|----------|--|--|--|
| Reactant | Ester | Cyanide | | | |
| Product | Aldehyde | Aldehyde | | | |
| $\xrightarrow{\text{LiAlH}_4-\text{THF}} \text{Ph-CH}_2-\text{CH}_2-\text{CH}_2\text{OH} + \text{C}_2\text{H}_5\text{OH}$ | | | | | |

$$\xrightarrow{\text{DIBAL-H}}$$
 Ph-CH=CH-CHO+C₂H₅OH

(b) By DIBAL at ordinary temperature esters are reduced to alcohols but at low temperature esters are reduced to aldehyde.

$$C_{6}H_{5}-C-OCH_{3} \xrightarrow{\text{DIBAL}} C_{6}H_{5}CH_{2}OH$$

$$\xrightarrow{\text{II}} C_{6}H_{5}-C-OCH_{3} \xrightarrow{\text{IIBAL}} C_{6}H_{5}CHO$$

$$\xrightarrow{\text{DIBAL}} C_{6}H_{5}CHO$$

(c) LAH reduce RCN to amine but DIBAL is found to be reduce it to aldehyde.

$$CH_{3}-C=N \xrightarrow[-]{LiAIH_{4}-THF} CH_{3}-CH_{2}-NH_{2}$$

$$CH_{3}-C=N \xrightarrow[-]{DIBAL} CH_{3}-CHO$$

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1.4 Miscellaneous reductions :

(i) By Red P & HI :

Used to prepare alkane from carbonyl compounds and alcohols generally.

(a)
$$R - C - R \xrightarrow{Red P + HI} A R - CH_2 - R$$

(b) $CH_3CH=O \xrightarrow{Red P + HI} CH_3CH_3$
(c) $R - CH_2OH \xrightarrow{Red P + HI} A R - CH_3$
(d) $CH_3 - CH - CH_3 \xrightarrow{Red P + HI} CH_3CH_2CH_3$

(ii) Meerwein-Pondorf-Verley reduction (MPV reduction) (Reduction by isopropyl alcohol and aluminium isopropoxide): It is selective reduction of ketones to alcohol, even in presence of other functional groups using Aluminium isopropoxide in isopropyl alcohol.



(iii) Wolff-kishner reduction [NH₂NH₂ / KOH] :

Used to prepane alkane from carbonyl compounds

$$\sum_{\substack{\mathbf{V} \\ \mathbf{V} \\ \mathbf{S}p^2}} O \xrightarrow{\mathbf{NH}_2 - \mathbf{NH}_2 / \mathbf{KOH}}_{\text{Using high boiling}} \xrightarrow{\mathbf{CH}_2}_{\substack{\mathbf{V} \\ \mathbf{S}p^3}} ; \qquad \mathsf{RCHO} \xrightarrow{\mathbf{NH}_2 \mathbf{NH}_2 / \mathbf{KOH}}_{\Delta} \xrightarrow{\mathbf{RCH3}}$$

Mechanism :

$$\sum_{\substack{i \in O \\ i \in P^{2} \\ i$$

Note : Wolff-kishner reduction is avoid to use for compounds which have **base sensitive** groups. [Like : Halogens, Acid halide, Esters, Anhydride]

Section (C) : Oxidation-1 Introduction

1. oxidation is defined as the addition of oxygen (electronegative) element to a substance or removal of hydrogen (electropositive) element from a substance.

or

2. Oxidation of an organic molecule usually corresponds to increasing its oxygen content or decreasing its hydrogen content.

$$\operatorname{RCH}_{2}\operatorname{OH} \xrightarrow{(O)} \operatorname{R} - \overset{O}{\operatorname{CH}} \xrightarrow{(O)} \operatorname{R} - \overset{O}{\operatorname{CH}} \xrightarrow{(O)}$$

3. Oxidation of an organic compound may be more broadly defined as a reaction that increases its content of any element more electronegative than carbon.

Ar-CH₃
$$\xleftarrow{(O)}{\longleftarrow}$$
 ArCH₂CI $\xleftarrow{(O)}{\longleftarrow}$ ArCHCl₂ $\xleftarrow{(O)}{\longleftarrow}$ ArCCl₃

When organic compound is oxidised, **oxidising agent** used is reduced. When an organic compound is reduced, the **reducing agent** used must be oxidized.

2.1 Oxidation of alkanes

Different products are formed by the use of different oxidising agents or different reaction conditions.

(i) Chemical oxidation with KMnO₄ or K₂Cr₂O₇: Alkanes are usually not affected by oxidising agents like KMnO₄ or K₂Cr₂O₇. However, alkanes having tertiary hydrogen are oxidised by these oxidising agents to an alcohol.

 $\begin{array}{c} (CH_3)_3CH \xrightarrow{KMnO_4} (CH_3)_3COH \\ (Isobutane) & (Tertiary butyl alcohol) \end{array}$

Ex. (i) $2CH_4 + O_2 \xrightarrow{Cu/523K/1000atm} 2CH_3OH$ (methanol) 9:1

(ii) CH₄ + O₂ $\xrightarrow{Mo_2O_3}$ HCHO + H₂O

(iii) $2CH_3-CH_3 + 3O_2 \xrightarrow{(CH_3COO_2)Mn} 2CH_3COOH + 2H_2O$

(iv)
$$CH_4 + O_2 \xrightarrow{Burn} C_{arbon} + 2H_2O$$

limited

2.2 Oxidation of alkenes and alkynes

(i) Baeyer reagent [cold diluted to 1% alkaline KMnO₄ solution] :

| Baeyer Reagent | Baeyer Reagent | Baeyer Reagent |
|----------------|----------------|----------------|
| Reactant | Alkene | Alkyne |
| Product | Vicinal diol | Diketone |
| | | |

Stereochemistry : syn addition.

Both-OH groups are add from same stereochemical side.

General Reaction



Stereochemistry : syn addition.







(iv) Oxidation with acidic KMnO₄ [KMnO₄/H⁺] : Stereochemistry : syn addition. When alkene & alkyne heated with KMnO₄ in acidic or in alkaline medium; following changes takes place

| KMnO₄/H⁺ | KMnO₄/H⁺ | KMnO₄/H⁺ | KMnO₄/H⁺ | KMnO₄/H⁺ | KMnO₄/H⁺ |
|----------|--------------------------|----------------------|---|-----------------|-----------------|
| Reactant | .= CH ₂ group | .= CH R group | .= CR ₁ R ₂ group | .≡ CH group | .≡ CR group |
| Product | CO ₂ | RCOOH | $O = CR_1R_2$ group | CO ₂ | RCOOH |
| | Carbon dioxide | Carboxylic acid | Ketone | Carbon dioxide | Carboxylic acid |

Ex. RCH=CH₂ $\xrightarrow{[0]}$ CO₂ + H₂O + RCOOH

Ex. RC=CH $\xrightarrow{[0]}$ CO₂ + H₂O + RCOOH

Ex. RC=C-R
$$\xrightarrow{[0]}$$
 2RCOOH

w



(v). Oxidation with ozone (ozonolysis) : Alkene & Alkyne

Like permanganate ozone cleaves double at very low temperature ($\approx -78^{\circ}$ C) bonds to give Ketones and aldehydes. However, ozonolysis is milder, and both Ketones and aldehydes can be recovered without further oxidation.

| Reductive Ozonolysis Products (O ₃ /Zn, H ₂ O) | | | | | | |
|--|--------------------------------------|---------------|--------------------------------------|-------------------|--------------------------------------|--|
| O ₃ /Zn, H ₂ O | O ₃ /Zn, H ₂ O | O₃/Zn, H₂O | O ₃ /Zn, H ₂ O | O₃/Zn, H₂O | O ₃ /Zn, H ₂ O | |
| Reactant | = CH ₂ group | = CH R group | $= CR_1 R_2 group$ | ≡ CH group | \equiv CR group | |
| Product | НСНО | O = CHR group | $O = CR_1R_2$ group | О -С-СНО | diketone | |
| | Formaldehyde | Aldehyde | Ketone | Keto aldehyde | diketone | |

| Oxidative Ozonolysis Products | | | | | | | |
|-------------------------------|---|---|---|---|---|--|--|
| O_3/H_2O_2 | O ₃ /H ₂ O ₂ | | |
| Reactant | =CH ₂ group | =CH R group | $= CR_1R_2$ group | =CH group | ≡CR group | | |
| Product | CO ₂ | RCOOH | O=CR ₁ R ₂ group | CO ₂ | RCOOH | | |
| | Carbon dioxide | Carboxylic acid | Ketone | Carbon dioxide | Carboxylic acid | | |

- **Ex.** C_8H_{10} (A) $\xrightarrow{O_3, H_2O}$ $C_4H_6O_2$ Acid (B). Identify (A) and (B) in the above reaction
- Sol.
 (A)
 C≡C
 (B)
 COOH
- **Ex.** A certain hydrocarbon has the formula $C_{16}H_{26}$. Ozonolysis followed by hydrolysis gives $CH_3(CH_2)_4CO_2H$ and succinic acid as the only product. What is hydrocarbon **Sol.** DU = 4
 - Molecular structure must be: $CH_3(CH_2)_4C \equiv C CH_2 CH_2 C \equiv C(CH_2)_4 CH_3$

Section (D) : Oxidation-2

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2.3 Oxidation reaction of alcohols :

| Oxidation Product of Alcohol-1 | | | | | | |
|------------------------------------|----------|------------|-----------------------------------|---|----------|------------|
| | We | ak oxidisi | ng agent | Strong oxidising agent | | |
| | PCC* | PDC** | CrO ₃ /Inert medium | CrO ₃ in water or H ₂ CrO ₄ | KMnO₄/H⁺ | K₂Cr₂O7/H⁺ |
| 1º alcohol or primary alcohol | Aldehyde | | Carboxylic acid | | | |
| 2º alcohol or secondary alcohol | Ketone | | Ketone | | | |
| 3º alcohol or tertiary alcohol | | Not oxidi | ised | Not oxidised | | |

(a) Pyridinium Chloro Chromate (PCC)

$$(\bigcirc_{N} + HCI + CrO_3 \xrightarrow{\text{Non aqueous solvent}} (\bigcirc_{H} .CI^-.CrO_3$$

- (b) Pyridinium dichromate (PDC) = $(2C_6H_5N.CrO_3)$
- (c) Jones reagent = dilute chromic acid + acetone
- (d) Collin's Reagent = CrO_3 + pyridine, CH_2CI_2
- (e) MnO₂ = It is selectively oxidised reagent & oxidised allylic and benzylic alcohol into aldehyde and ketone.

| Oxidation Product of Alcohol-2 | | | | | | |
|--|---|----------|--|--|--|--|
| | Very-Very Strong oxidising agent KMnO₄/H+/Heat | | | | | |
| 1º alcohol or Primary alcohol | Carboxylic acid | Aldehyde | | | | |
| 2º alcohol or Secondary alcohol | Mixture of Carboxylic acid | Ketone | | | | |
| 3º alcohol or tertiary alcohol Mixture of Carboxylic acid Dehydrate to | | | | | | |
| $CH_3 - CH_2 - CH_2 - OH \xrightarrow{Cu/\Delta} CH_3 - CH_2 - CH = O$ (dehydrogenation) | | | | | | |

| CH₃ – CH – CH₃ I OH | $\xrightarrow{Cu/\Delta} CH_{3} - C - CH_{3}$ | (dehydrogenation) |
|--|---|---------------------------------|
| CH ₃ CH ₃ - C - CH ₃ | $ \begin{array}{c} Cu/\Delta & CH_3 \\ I \\ (-H_2O) \end{array} \rightarrow CH_3 - C = CH_2 \end{array} $ | [dehydration (Reduced Product)] |

Oppenaur's oxidation

(i) This reaction involves the oxidation of a secondary alcohol with a ketone and base to the corresponding ketone.

(ii) Commonly used bases are aluminium tert-butoxide.

 $\begin{array}{c} \mathsf{R}_2\mathsf{CHOH} + (\mathsf{CH}_3)_2\mathsf{CO} \xleftarrow{\mathsf{Al}(\mathsf{OCMe}_3)_3}{} \mathsf{R}_2\mathsf{CO} + \mathsf{CH}_3\mathsf{CH}(\mathsf{OH})\mathsf{CH}_3\\ 2^{\mathrm{o}} \, \mathsf{Alcohol} \, \, \mathsf{Acetone} \, \mathsf{CO} + \mathsf{CH}_3\mathsf{CH}(\mathsf{OH})\mathsf{CH}_3\\ \mathsf{Acetone} \, \mathsf{CO} + \mathsf{CH}_3\mathsf{CH}(\mathsf{OH})\mathsf{CH}_3\\ \mathsf{CH}(\mathsf{OH})\mathsf{CH}_3\\ \mathsf{CH}(\mathsf{OH})\mathsf{CH}_3\\ \mathsf{CH}(\mathsf{OH})\mathsf{CH}_3\\ \mathsf{CH}(\mathsf{OH})\mathsf{CH}_3\\ \mathsf{CH}(\mathsf{OH})\mathsf{CH}_3\\ \mathsf{CH}(\mathsf{OH})\mathsf{CH}_3\\ \mathsf{CH}(\mathsf{OH})\mathsf{CH}_3\\ \mathsf{CH}(\mathsf{OH})\mathsf{CH}_3\\ \mathsf{CH}(\mathsf{OH})\mathsf{CH}_3\\ \mathsf{CH}(\mathsf{CH})\mathsf{CH}_3\\ \mathsf{CH}(\mathsf{CH})\mathsf{CH}_3\\ \mathsf{CH}(\mathsf{CH})\mathsf{CH}_3\\ \mathsf{CH}(\mathsf{CH})\mathsf{CH}(\mathsf{CH})\mathsf{CH}_3\\ \mathsf{CH}(\mathsf{CH})\mathsf{CH}_3\\ \mathsf{CH}(\mathsf{CH})\mathsf{CH}_3\\ \mathsf{CH}(\mathsf{CH})\mathsf{CH}(\mathsf{CH})\mathsf{CH}_3\\ \mathsf{CH}(\mathsf{CH})\mathsf{CH}_3\\ \mathsf{CH}(\mathsf{CH})\mathsf{CH}_3\\ \mathsf{CH}(\mathsf{CH})\mathsf{CH}(\mathsf{CH})\mathsf{CH}_3\\ \mathsf{CH}(\mathsf{CH})\mathsf{CH}(\mathsf{CH})\mathsf{CH}_3\\ \mathsf{CH}(\mathsf{CH})\mathsf{CH}(\mathsf{CH})\mathsf{CH})$

Rate of Oxidation :

(b) RCHO > RCH₂OH

Ex. Write the product of following reactions.

(a) $RCH_2OH > R_2CHOH > R_3C-OH$ (inert)

$$CH_{3}-CH=CH-CH_{2}-CH_{2}-OH$$

$$(X)$$

$$X \xrightarrow{K_{2}Cr_{2}O_{7}} (1) H_{2}SO_{4} CH_{3} - CH_{2} - OH + HOOC - C - CH_{2} - CH_{2} - OH$$

$$X \xrightarrow{PCC} (2) CH_{3}-CH=CH - C - CH_{2} - CHO$$

$$X \xrightarrow{\text{Oppenauer oxidation}} CH_3 - CH = CH - CH_2 - CHO$$

$$(3) \xrightarrow{\text{CrO}_2} / aq$$

$$X \xrightarrow{(4) \text{ acetone}} CH_3 - CH = CH - CH_2 - COOH$$

$$X \xrightarrow{(4) \text{ acetone}} CH_3 - CH = CH - C - CH_2 - CH_2 - OH$$

$$\|$$

$$(5) \qquad \|$$

2.4 **Oxidation reaction of carbonyl compound** Acidic KMnO₄ & K₂Cr₂O₇ as oxidising agent : (i)

Aldehydes are oxidised to carboxylic acid having same number of C atoms as aldehyde. $HCHO + [O] \longrightarrow HCOOH$ $RCHO + [O] \longrightarrow RCOOH$; Ketones are oxidised with difficulty. They are oxidised only on heating with a strong oxidising agent. Ö

$$CH_{3} - \overset{[]}{C} - CH_{3} + [O] \xrightarrow{Cr_{2}O_{7}^{2-} + H^{+}} CH_{3}COOH + CO_{2} + H_{2}O$$

. .

In case of mixed or unsymmetrical ketones the >C = O group remains with the smaller alkyl group. (Popoff's rule)

 $CH_{3}COCH_{2}CH_{3} \xrightarrow{[O]} 2CH_{3}COOH ; CH_{3}COCH_{2}CH_{2}CH_{3} \xrightarrow{[O]} CH_{3}COOH + CH_{3}CH_{2}COOH$

Mechanism (with Cr⁺⁶ oxidising agents):
(i) CrO₃ + H₂O
$$\rightarrow$$
 H₂CrO₄ = $\begin{bmatrix} HO - Cr - OH \\ HO - Cr - OH \\ H \end{bmatrix}$
(ii) R - $\begin{pmatrix} H \\ - OH + H - O \\ H \end{pmatrix}$ + $\begin{pmatrix} O \\ - OH - H \\ - OH \end{pmatrix}$ + $\begin{pmatrix} H \\ - H_2O \\ - H_2O \end{pmatrix}$ + $\begin{pmatrix} H \\ - H_2O \\ - H_2O \end{pmatrix}$ + $\begin{pmatrix} H \\ - H_2O \\ - H_2O \end{pmatrix}$ + $\begin{pmatrix} H \\ - H_2O \\ - H_2O \end{pmatrix}$ + $\begin{pmatrix} H \\ - H_2O \\ - H_2O \end{pmatrix}$ + $\begin{pmatrix} H \\ - H_2O \\ - H_2O \end{pmatrix}$ + $\begin{pmatrix} H \\ - H_2O \\ - H_2O \end{pmatrix}$ + $\begin{pmatrix} H \\ - H_2O \\ - H_2O \end{pmatrix}$ + $\begin{pmatrix} H \\ - H_2O \\ - H_2O \end{pmatrix}$ + $\begin{pmatrix} H \\ - H_2O \\ - H_2O \end{pmatrix}$ + $\begin{pmatrix} H \\ - H_2O \\ - H_2O \end{pmatrix}$ + $\begin{pmatrix} H \\ - H_2O \\ - H$

Remarks :

(1) Primary alcohol forms a chromate ester with chromic acid.

- (2) The chromate ester decomposes in 2^{nd} slow step with the elimination of α -hydrogen. So the first oxidation product, an aldehyde is obtained.
- (3) In **aqueous medium**, aldehyde forms a gemdiol (hydrated aldehyde). It is further oxidised to an acid by similar mechanism.

(4) The following reactivity orders can be explained by this mechanism :

Rate of Oxidation

(a) $R-CH_2OH > R-CD_2OH$ (Bond Energy : C-H < C-D) (b) RCHO > RCDO

(ii) With Tollen's reagent :

RCHO (aldehydes) can be easily oxidised to RCOOH (except HCHO that can be oxidised to CO_2) by weak oxidising agents like ammonical AgNO₃ (**Tollen's reagent**) hence they are better reducing agents.

Aldehydes reduce Tollen's reagent to Ag and appears in the form of silver mirror is called **silver-mirror test.** It is given by all aldehydes and reducing sugars.

 $\mathsf{RCHO} + 2[\mathsf{Ag}(\mathsf{NH}_3)_2^+] + 3\mathsf{OH}^- \xrightarrow{\Lambda} \mathsf{RCOO}^- + 2\mathsf{Ag} \downarrow + 4\mathsf{NH}_3 + 2\mathsf{H}_2\mathsf{O}$

(iii) With Fehling solution :

Aldehydes (except benzaldehyde) reduce **Fehling's** solution (Cu^{2+} reduced to Cu^+) which is an alkaline solution of cupric (Cu^{2+}) ion complexed with tartrate ion.

 $\mathsf{RCHO} + 2\mathsf{Cu}^{2+} + 3\mathsf{OH}^{-} \xrightarrow{\Delta} \mathsf{RCOO}^{-} + \frac{\mathsf{Cu}_2\mathsf{O} \quad \downarrow}{\mathsf{red} \quad \mathsf{ppt.}} + 2\mathsf{H}_2\mathsf{O}$

Aldehydes also reduce Benedict's solution (Cu2+ complexed with citrate ion) to Cu+

(iv) With Benedict's solution

Sodium citrate + NaOH + NaHCO₃ + CuSO₄ RCHO + Cu²⁺ $\xrightarrow{H_2O}_{\Delta}$ RCOOH + Cu^{\oplus} \downarrow \downarrow RCOO⁻ Cu₂O(red ppt.) RCHO + HgCl₂ + H₂O $\xrightarrow{}_{\Delta}$ RCOOH + 2HCl + Hg₂Cl₂

RCHO + Hg₂Cl₂ + H₂O → RCOOH + 2HCl + 2Hg \downarrow grey ppt.

(v) With Schiff's reagent

Schiff's Reagent is aq. solution of following base decolourised by passing SO₂. Aldehyde restore pink colour of Schiff's reagent.



 $\xrightarrow{SO_2}$ Colourless solution (Schiff's Reagent) \xrightarrow{RCHO} RCOOH + Pink colour

p-Rosaniline Hydrochloride

[⊕]NH₂Cl[⊖]

Magenta colour (Fuschin)

Ketons are not easy to oxidize so they do not give these 5 tests. These five tests can be used to distinguish aldehyde and ketones. Both gives 2, 4 DNP test.

(vi) Oxidation by using SeO₂

SeO₂ is a selective oxidizing agent with converts –CH₂–group adjacent to carbonyl group into carbonyl group. The reagent, in general, oxidises active methylene and methyl groups to ketonic and aldehydic groups respectively.



(vii) Baeyer-villiger oxidation

Baeyer-villiger oxidation is the oxidative cleavage of a carbon-carbon bond adjacent to a carbonyl which converts ketones to esters and cyclic ketones to lactones.

It can be carried out with peracids such as MCBPA, or with hydrogen peroxide and a lewis acid.



KETONES ARE DIFFICULT TO OXIDIZE :

Ketones can be oxidized from their enolic form at high temperature with very strong oxidizing agent. Oxidation of ketones is sometimes governed by Popoff's rule. According to this rule carbonyl group remains with the smaller alkyl group. More electron rich alkene will be easy to oxidized.

$$Me - C - Me \xrightarrow{[0]} MeCOOH + CO_2 + H_2O$$

2.5 Oxidation reaction of diols

(i) HIO₄ oxidation : (Oxidation by lead acetate is similar to HIO₄ oxidation)

Mechanism :



cyclic periodate ester

Remarks

(1) HIO₄ (periodic acid) oxidises vicinal diols (1, 2-diols).

(2) It brings about oxidative cleavage of vicinal diol.

(3) It can also oxidise α -hydroxy carbonyl compound and α -dicarbonyl compound.

(4) HIO₄ forms a cyclic periodate ester as an intermediate. So the two –OH groups should have synconformation.

(5) In cyclic diols only cis-vicinal diols are oxidised. Trans isomers are not oxidised.

Ex. General reaction

Ex.

Section (E) : Hydrolysis

Introduction :

Hydrolysis is a chemical reaction or process in which a **molecule splits into two parts** by reacting with a molecule of water, (H₂O). One of the parts gets OH^- from the water molecule and the other part gets H^+ from the water. Such reactions are endothermic.

This is distinct from a hydration reaction, in which water molecules are added to a substance, but no fragmentation of molecule/species occurs. Such a process is exothermic.

(i) Hydrolysis of an ester :

(b)

Hydrolysis of an ester involves breaking off an ester link. It can takes place in



(a) Mild acidic medium : Dilute H₂SO₄, dilute HCl.

Strong alkaline medium : Aqueous NaOH or KOH and heat.

One hydrolysis product contains a hydroxyl functional group, while the other contains a carboxylic acid functional group.



(ii) Hydrolysis of an anhydride :

The hydrolysis of acid anhydride produces two carboxylic acids.

(iii) Hydrolysis of acid halide :

Hydrolysis of an acid halide results into a carboxylic acid and hydrogenhalide. Only the carboxylic acid product has a hydroxyl group derived from the water. Hydrohalic acid product gains the remaining hydrogen ion.

$$R - C + CI \xrightarrow{H \to 0} R - C - OH + HCI$$

(iv) Hydrolysis of acid amide :

Hydrolysis of an amide results into a carboxylic acid and an amine product or ammonia, only the carboxylic acid product has a hydroxyl group derived from the water. The amine product (or ammonia) gains the remaining hydrogen ion.

$$R - C + NH_{2} + NH_{2} + R - C - OH + NH_{3}$$

(v) Hydrolysis of cyanides :

Cyanide on hydrolysis produce ammonia and carboxylc acids. It is carried out in acidic medium generally but hydrolyse in basic medium also.

$$R - C \neq N \xrightarrow{3H^{O} H, H^{+}} R - C \xrightarrow{H} OH + NH_{3}$$

