Aldehydes & Ketones - 09

Chemical properties - 4

i) Tollen's Test
ii) Fehling's Test

Aldehydes are easily oxidised to corresponding Carboxylic Acids with strong as well as mild oxidising agents

$$R\text{-}CHO \xrightarrow{[O]} R\text{-}COOH$$

Strong Oxidising agent → HNO_3, acidified $K_2Cr_2O_7$, acidified $KMnO_4$, etc

Mild oxidising agent → Tollen's Reagent, Fehling's Reagent

Ketones are oxidised at high temperature only by strong oxidising agent and not by mild oxidising agents.

i) Tollen's Test: (Silver Mirror Test)

Tollen's Reagent: Ammoniacal Silver Nitrate

$$AgNO_3 \xrightarrow{NH_4OH} Ag_2O \xrightarrow{NH_4OH} [Ag(NH_3)_2]^+ OH^-$$

Ag_2O: PPt forms & redissolves

$[Ag(NH_3)_2]^+ OH^-$: Tollen's Reagent

Freshly prepared

$$R\text{-}CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \xrightarrow{\text{Basic medium}} RCOO^- + 2Ag + 2H_2O + 4NH_3$$

$Ag^+ \longrightarrow Ag$ (Reduction)

ppt of Metallic Silver formed deposist as a mirror

⇒ Silver Mirror Test

$CH_3-CHO \xrightarrow{T.R} CH_3COO^- + Ag$ ✓

$C_6H_5-CHO \xrightarrow{T.R} C_6H_5COO^- + Ag$ ✓

This test is shown by aliphatic as well as Aromatic aldehydes

*** Ketones do not show this Silver Mirror Test or Tollen's Test

But α-hydroxy ketones do

$$CH_3-\overset{O}{\overset{\|}{C}}-\overset{\alpha}{CH}(OH)-CH_3 \xrightarrow[-H_2O]{T.R\ [O]} CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$$

diketo

Formic acid also gives Positive Tollens Test

$$HCOOH \xrightarrow{T.R\ [O]} CO_2 + H_2O + Ag$$

Silver Mirror

Terminal alkynes also show Tollen's Test But do not form Silver mirror Test

$$CH_3-C\equiv C-H \xrightarrow{T.R.} CH_3-C\equiv C^-Ag^+$$

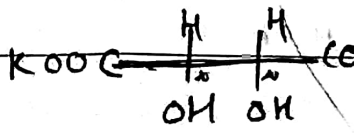
$$CH\equiv CH \xrightarrow{T.R} CH\equiv C^-Ag^+ \text{ (white ppt.)}$$

ii) Fehling's Solution Test:

equal mixture of Fehling Solution A + Fehling Solution B

Fehling Solution A → aq Copper sulphate $CuSO_4.5H_2O$ (Blue)

Fehling Solution B → Sodium potassium salt of tartaric acid (Rochelle Salt)



- $R-CHO + 2Cu^{2+} + 5OH^- \longrightarrow RCOO^- + Cu_2O + 3H_2O$

aldehyde — Reddish brown ppt

$Cu^{2+} \longrightarrow Cu^{+1}$

Cupric blue — Cuprous Reddish brown

Note: Aromatic aldehydes do not give positive Fehling's Solution test as

Fehling solution is very weak oxidising agent