12. CANNIZARO REACTION

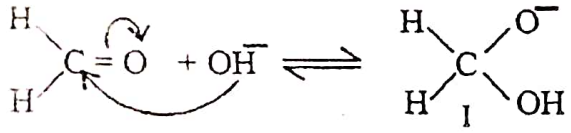
Aldehydes having no α -hydrogen atom when treated with concentrated solution of alkali (50% NaOH or KOH) undergo self oxidation and reduction forming the corresponding acid and alcohol. This reaction is known as ***cannizaro reaction***. E.g. Thus formaldehyde and trimethyl acetaldehyde react as under.

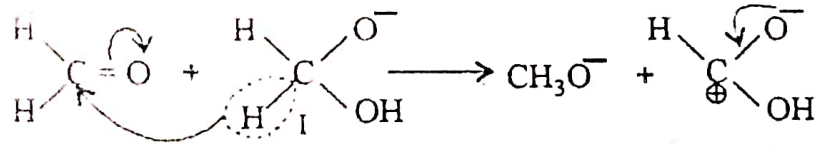
$$\underset{\text{Formaldehyde}}{2HCHO} + KOH \longrightarrow \underset{\text{Potassium formate}}{HCOOK} + \underset{\text{Methyl alcohol}}{CH_3OH}$$

$$(CH_3)_3C\,CHO + KOH \longrightarrow (CH_3)_3C\,COOK + + (CH_3)_3C\,CH_2OH$$

Mechanism

1) Nucleophilic addition of hydroxyl ion (OH^-) on the carbonyl group gives complex anion I.
2) The anion I transfers a hydride (H^-) ion to another molecule of formaldehyde reducing it to methoxide ion (CH_3O^-) while the anion I itself is oxidised to formic acid.





Thus we get CH_3O^- and HCOOH. The resulting methoxide ion and formic acid exchange a proton to form the methyl alcohol and formate ion.

$$CH_3O^- + HCOOH \longrightarrow CH_3OH + HCOO^-$$

The aliphatic aldehydes generally have activated α-hydrogen atoms. So the Cannizaro reaction is rare with aliphatic aldehydes The reaction is more common among the aromatic aldehydes.

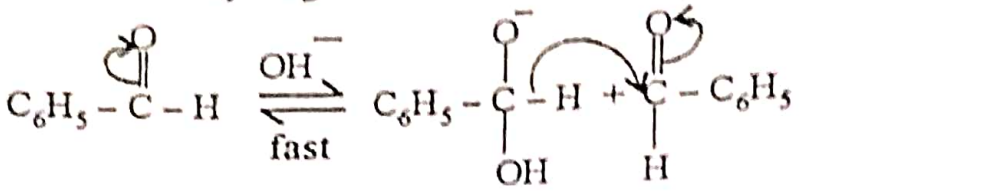
Benzaldehyde on treatment with NaOH, does not give a resin, but undergoes Cannizaro reaction. Usually aldehydes with no α-hydrogen undergo Cannizaro reaction.

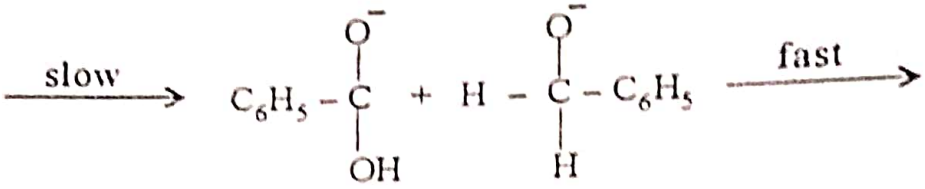
$$2C_6H_5CHO + NaOH \longrightarrow C_6H_5COONa + C_6H_5CH_2OH$$

Benzaldehyde — Sodium benzoate — Benzyl alcohol

Machanism

It involves hydrogen ion transfer. It is as follows.





$$C_6H_5COO^- + C_6H_5CH_2OH$$

The Cannizaro reaction can also take place between two different aldehydes and is known as *'Crossed Cannizaro'* reaction.

$$C_6H_5CHO + HCHO + NaOH \longrightarrow C_6H_5CH_2OH + HCOONa$$

Benzaldehyde — Formaldehyde — Benzyl alcohol — Sodium Formate

Significance

(i) This reaction is used to distinguish between formaldehyde and other aldehydes (Other aldehydes give resins with conc. NaOH)

(ii) This reaction involves ***auto-oxidation and auto reduction***. In presence of NaOH one molecule of formaldehyde is oxidised to formic acid while another molecule is reduced to methyl alcohol.

13. HALOFORM REACTION

When a methyl ketone CH_3CO is treated with a halogen in sodium hydroxide solution it is oxidised to a carboxylic acid containing one carbon less than the original molecule. Simultaneously a trihalomethane is formed. This reaction is known as ***Haloform reaction***.

Compounds containing CH_3CO group or which could be easily converted into compounds with CH_3CO group undergo haloform reaction.

$$R-\overset{O}{\overset{\|}{C}}-CH_3 + 3Br_2 + 4\,NaOH \longrightarrow R-\overset{O}{\overset{\|}{C}}-ONa + CHBr_3 + 3H_2O + 3NaBr \quad 3)$$

This reaction takes place in two stages. First the three hydrogen atoms methyl group are replaced by three halogen atoms. Then the molecule is cleaved to give an acid and trihalomethane.

$$R-\overset{O}{\overset{\|}{C}}-CH_3 + 3Br_2 + 3NaOH \longrightarrow R-\overset{O}{\overset{\|}{C}}-CBr_3 + 3H_2O + 3NaBr$$

$$R-\overset{O}{\overset{\|}{C}}-CBr_3 + NaOH \longrightarrow R-\overset{O}{\overset{\|}{C}}-ONa + \underset{\text{Bromoform}}{CHBr_3}$$

The reaction yileds trihalomethanes-chloroform, bromoform or iodoform depending on the halogen used.

i $$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[[O]]{I_2 / NaOH} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

$$\xrightarrow{I_2} \underset{\substack{\text{Tri iodo}\\ \text{acetaldehyde}}}{CI_3CHO} \xrightarrow{NaOH} \underset{\text{Iodoform}}{CHI_3} + \underset{\substack{\text{Sodium}\\ \text{formate}}}{HCOONa}$$

ii $$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{I_2} CI_3CHO \xrightarrow{NaOH} CHI_3 + HCOONa$$

iii $$\underset{\text{Acetone}}{CH_3COCH_3} \xrightarrow{I_2} CI_3COCH_3 \xrightarrow{NaOH} CHI_3 + \underset{\substack{\text{Sodium}\\ \text{acetate}}}{CH_3COONa}$$

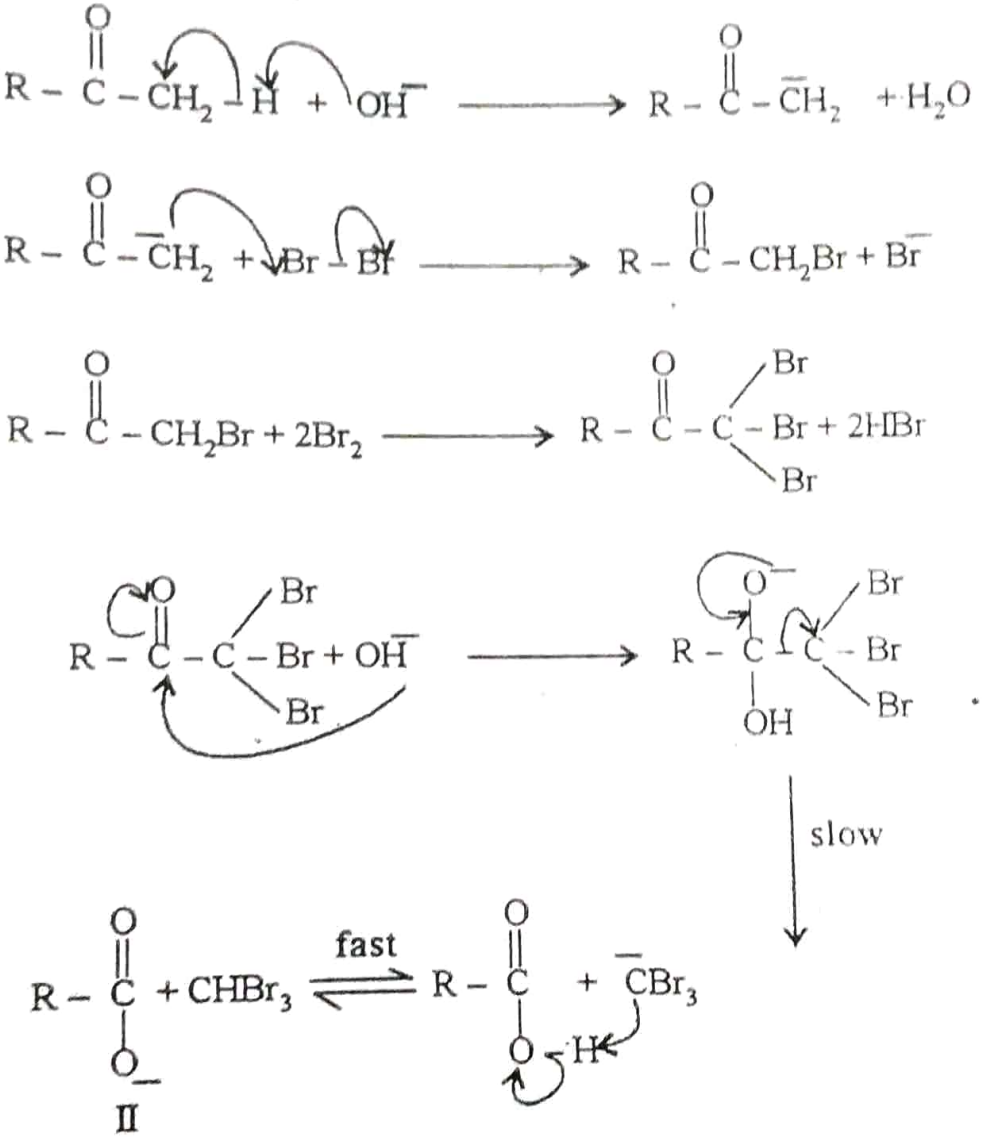
(We can write similar equations for chloroform or Bromoform. For Chloroform replace I with Cl and for bromoform replace with Br).

Mechanism

1) One hydrogen atom of the CH_3 group is replaced by halogens in alkali solution. Due to the electron with drawing effect of the halogen (Br) atom, the remaining two hydrogen atoms of the methyl group become even more acidic. Thus the hydrogen atoms are successively replaced by halogen atoms.

2) Due to the inductive effect of the halogen atom's the positivity of the carbonyl carbon increases. The OH^- ion attacks to form the anion I.

3) The anion I then cleaves to give a molecule of iodoform and the carboxylate ion II.



Significance

(i) The haloform reaction helps to find the presence of $COCH_3$ group. The haloform reaction is useful for distinguishing methyl ketones from other ketones.

(ii) Iodoform test : Substance is treated with I_2 and NaOH. Yellow precipitate is formed with characteristic smell. This test is used to distinguish between methyl alcohol and ethyl alcohol (Ethyl alcohol answers this test) ; Acetaldehyde and benzaldehyde (acetaldehyde answers this test).

$$R-\overset{O}{\overset{\|}{C}}-CH_3 + 3Br_2 + 4NaOH \longrightarrow R-\overset{O}{\overset{\|}{C}}-ONa + CHBr_3 + 3H_2O + 3NaBr$$

This reaction takes place in two stages. First the three hydrogen atoms methyl group are replaced by three halogen atoms. Then the molecule is cleaved to give an acid and trihalomethane.

$$R-\overset{O}{\overset{\|}{C}}-CH_3 + 3Br_2 + 3NaOH \longrightarrow R-\overset{O}{\overset{\|}{C}}-CBr_3 + 3H_2O + 3NaBr$$

$$R-\overset{O}{\overset{\|}{C}}-CBr_3 + NaOH \longrightarrow R-\overset{O}{\overset{\|}{C}}-ONa + CHBr_3$$

Bromoform

The reaction yileds trihalomethanes-chloroform, bromoform or iodoform depending on the halogen used.

i $CH_3CH_2OH \xrightarrow[[O]]{I_2 / NaOH} CH_3CHO$

Ethyl alcohol — Acetaldehyde

$$\xrightarrow{I_2} CI_3CHO \xrightarrow{NaOH} CHI_3 + HCOONa$$

Tri iodo acetaldehyde — Iodoform — Sodium formate

ii $CH_3CHO \xrightarrow{I_2} CI_3CHO \xrightarrow{NaOH} CHI_3 + HCOONa$

Acetaldehyde

iii $CH_3COCH_3 \xrightarrow{I_2} CI_3COCH_3 \xrightarrow{NaOH} CHI_3 + CH_3COONa$

Acetone — Sodium acetate

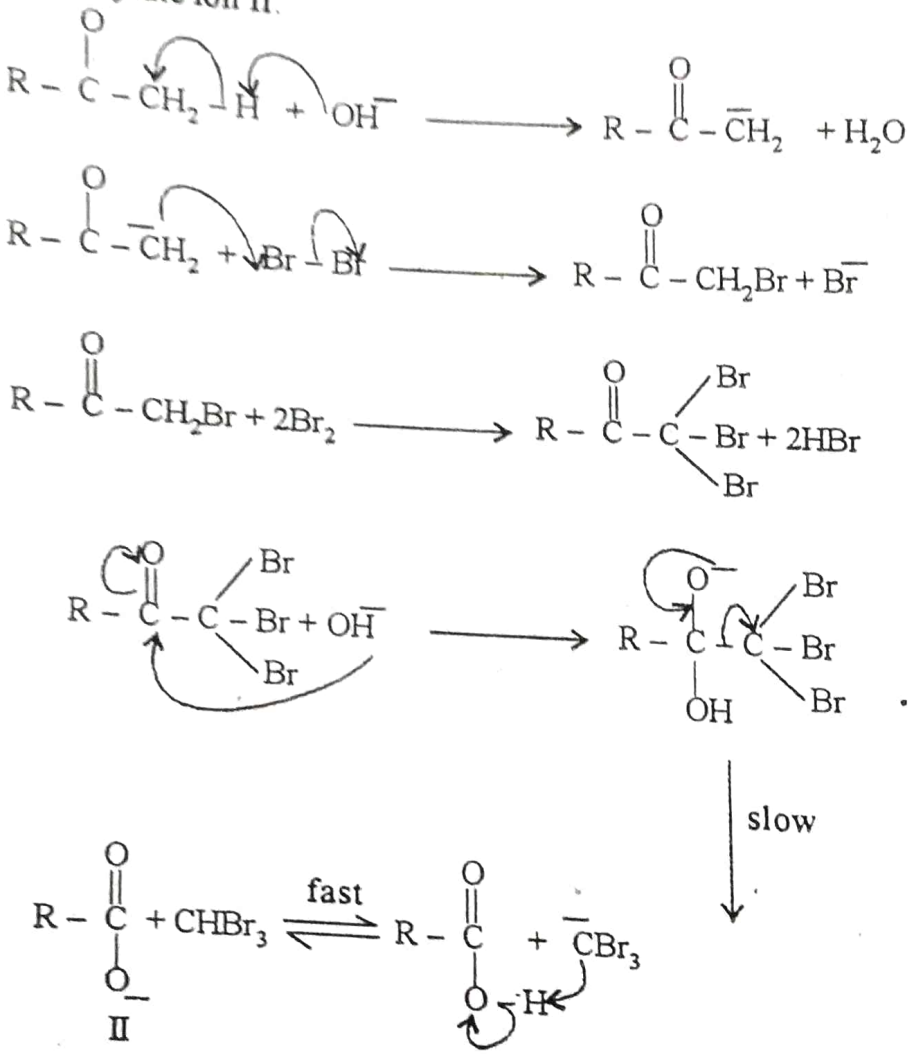
(We can write similar equations for chloroform or Bromoform. For Chloroform replace I with Cl and for bromoform replace with Br).

Mechanism

1) One hydrogen atom of the CH_3 group is replaced by halogens in alkali solution. Due to the electron with drawing effect of the halogen (Br) atom, the remaining two hydrogen atoms of the methyl group become even more acidic. Thus the hydrogen atoms are successively replaced by halogen atoms.

2) Due to the inductive effect of the halogen atom's the positivity of the carbonyl carbon increases. The OH^- ion attacks to form the anion I.

3) The anion I then cleaves to give a molecule of iodoform and the carboxylate ion II.



Significance

(i) The haloform reaction helps to find the presence of $COCH_3$ group. The haloform reaction is useful for distinguishing methyl ketones from other ketones.

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14. α, β –UNSATURATED COMPOUNDS - MICHAEL ADDITION

The addition of active methylene compound to α, β - unsaturated compounds in the presence of a basic catalyst is called Michael addition. Sodium ethoxide or piperidine is used as catalyst.

The addition of acetoacetic ester to acetonitrile is an example for this reaction.

$CH_2 = CH - CN + CH_3COCH_2COOC_2H_5 \longrightarrow$

acetonitrile EAA $CH_3 - CO - \underset{\underset{CH_2CH_2CN}{|}}{CH} - COO - C_2H_5$

Product

Acrolein undergoes, Michael reaction whe treated with diethy melonate in presence of piperidine or sodium ethoxide.

$CH_2 = CH - CHO + H_2C(COOC_2H_5)_2 \xrightarrow{NaOC_2H_5} CH_2 - CH_2 - CHO$ with $CH(COOC_2H_5)_2$

Acrolein — Diethyl malonate — Product

Mechanism :

$CH_2(COOC_2H_5)_2 \xrightarrow{NaOC_2H_5} \bar{C}H(COOC_2H_5)_2 + H^+$

$CH_2 = CH - \underset{\underset{H}{|}}{C} = \ddot{O} \longleftrightarrow {}^{+}CH_2 - CH = CH - \bar{O}$

$CH_2(COOC_2H_5)_2 + {}^{+}CH_2 - CH = CH - \bar{O} \longrightarrow \underset{\underset{CH(COOC_2H_5)_2}{|}}{CH_2 - CH = CH - \bar{O}}$

$\underset{\underset{CH(COOC_2H_5)_2}{|}}{CH_2 - CH = CH - OH} \xrightleftharpoons{H^+} \underset{\underset{CH(COOC_2H_5)_2}{|}}{CH_2 - CH_2 - CHO}$

Enolform — Ketoform

15. OPPENAUER OXIDATION :

This reaction is reverse of Meerwein - Pondorf - Verley reduction and is used for the oxidation of alcohols to ketones in the presence of aluminium tertiary butoxide in benzene or toluene solution. A large excess of a ketone, (acetone or cyclo hexanone) is generally used to make the reaction proceed in the desired direction.

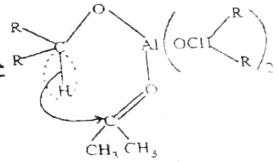
$\underset{\underset{R}{|}}{\overset{R}{|}}CHOH + CH_2 - \underset{\underset{O}{||}}{C} - CH_3 \xrightleftharpoons{Al[OC(CH_3)_2]_3} \underset{\underset{R}{|}}{\overset{R}{|}}C=O + (CH_3)_2CHOH$

This reaction also involves the transfer of a hydride ion via a cyclic complex as represented below.

$3\ \underset{\underset{R}{|}}{\overset{R}{|}}CHOH + Al\left[O - \underset{\underset{CH_3}{|}}{\overset{CH_3}{\overset{|}{C}}} - CH_3\right]_3 \rightleftharpoons \left[\underset{\underset{R}{|}}{\overset{R}{|}}CHO\right]_3 + Al + 3(CH_3)_3COH$

alcohol — aluminium tert. butoxide — tertiary butyl alcohol

$\left[\underset{\underset{R}{|}}{\overset{R}{|}}CHO\right]_3 + Al + CH_3COCH_3 \rightleftharpoons$



cyclic complex

$\longrightarrow \underset{\underset{R}{|}}{\overset{R}{|}}C=O + (CH_3)_2COAl(OCHR_2)_2$

ketone

PHOTO CHEMISTRY OF CARBONYL COMPOUNDS - NORRISH TYPE -I AND TYPE-II ONLY

Photochemical reactions of simple ketones and aldehydes which result in the fission of C—CO bond followed by elimination of CO are called *Norrish type I process*.

E.g., Vapour phase photolysis of acetone. The products depend upon the temperature of the experiment.

1. ***High temperatures :*** Ethane and CO are got

i. $CH_3COCH_3 \xrightarrow[V.P.]{h\nu} [CH_3COCH_3]^* \longrightarrow CH_3CO\bullet + \bullet CH_3$

ii. $CH_3CO\bullet \longrightarrow \bullet CH_3 + CO\uparrow$

iii. $\bullet CH_3 + \bullet CH_3 \longrightarrow C_2H_6$

2. *Room temperature* : Biacetyl, accetaldehyde, methane and some hexane 2,5, dione are got

i. $[CH_3COCH_3] \xrightarrow{h\nu} [CH_3COCH_3]^* \longrightarrow CH_3CO\bullet + \bullet CH_3$

ii $CH_3CO\bullet + \bullet OCCH_3 \longrightarrow CH_3COCOCH_3$

iii $CH_3CO\bullet + CH_3COCH_3 \longrightarrow CH_3CHO + \bullet CH_2COCH_3$

iv $CH_3\bullet + CH_3COCH_3 \longrightarrow CH_4 + \bullet CH_2COCH_3$

v $CH_3COCH_2\bullet + \bullet CH_2COCH_3 \longrightarrow CH_3COCH_2CH_2COCH_3$

Photochemical reactions of complicated ketones and aldehyde which result in an alkene and a lower ketone via the enol form by abstracting a γ hydrogen and undergoing fission is called ***Norrish type II process***. Here elimination of CO occurs to a lesser extent.

Here, the hydrogen atom at the γ carbon forms a six member cyclic transition involving the carbonyl oxygen as one of the member of the ring. E.g., Vapour phase hexane-2-one giving mainly propene and acetone.