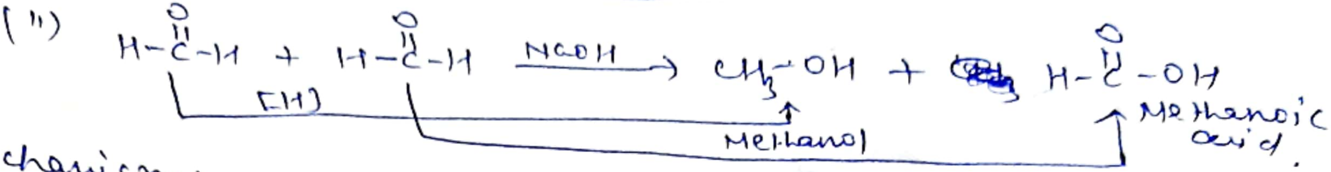
Cannizaro Reaction :-

Aldehydes having no α-hydrogen (like HCHO, ArCHO --etc) undergo disproportionation in the presence of concentrated caustic alkali solutions. One molecule of the aldehyde oxidises another to the acid and is itself reduced to primary alcohol. The reaction best proceeds with aromatic aldehydes.

e.g. (i)

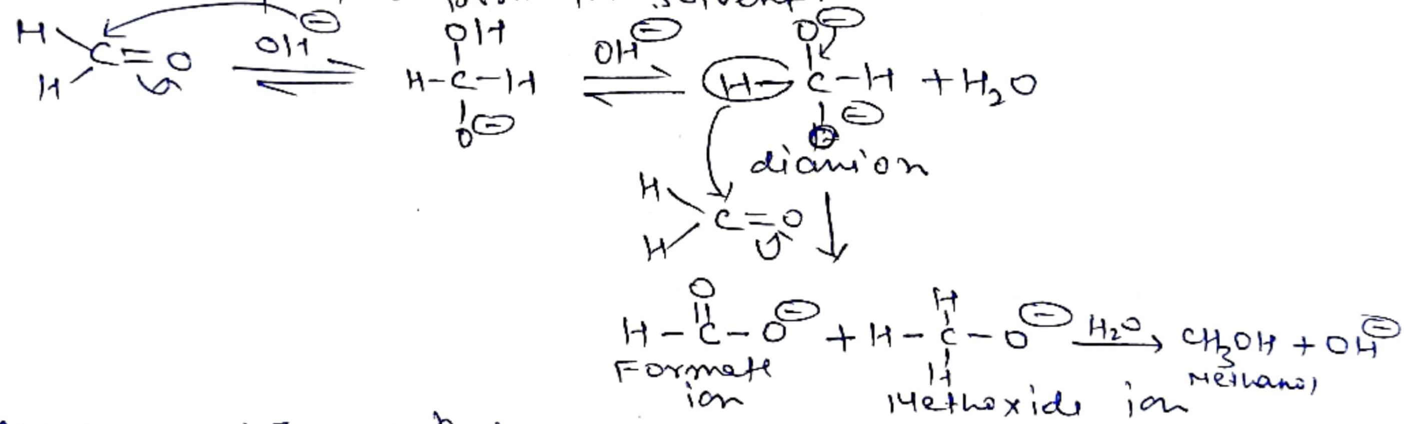
$$\underbrace{C_6H_5CHO + C_6H_5CHO}_{[H]\quad [O]} \xrightarrow{NaOH(conc.)} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Sod. benzoate}}{C_6H_5COONa}$$

(ii)



$$H-\overset{O}{\overset{\|}{C}}-H + H-\overset{O}{\overset{\|}{C}}-H \xrightarrow{NaOH} \underset{\text{Methanol}}{CH_3-OH} + \underset{\text{Methanoic acid}}{H-\overset{O}{\overset{\|}{C}}-OH}$$

Mechanism :- The first step of the reaction is reversible addition of $OH^{\ominus}$ ion to the $>C=O$ gr. resulting in the formation of hydroxyalkoxide, which also lose a proton in the basic solution to give dianion. The strong electron donating character of $O^{\ominus}$ makes the dianion much more powerful hydride ion donor, so it transfers its hydride ion directly to another aldehyde to yield acid & alkoxide ion. The alkoxide ion acquires a proton from the solvent.



Evidence · When rxn is carried out in presence of deutrated water (D_2O), no C-D bond is found in the resulting alcoho, as it would have been, if $H^{\ominus}$ ion had become free & it shows direct $H^{\ominus}$ transfer from one molecule to another.

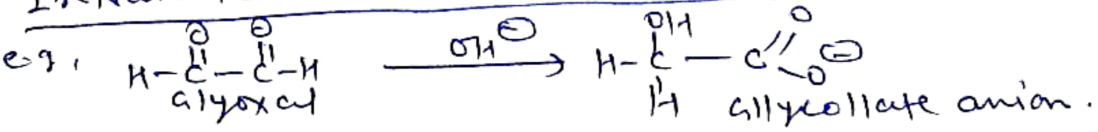
Extention & Application :-) When the cannizaro rxn is taking place between two different aldehydes, then it is called crossed -- . In such rxn, the more reactive aldehyde is generally oxidised.

e.g.

$$HCHO + ArCHO \xrightarrow{OH^{\ominus}} \underset{\text{Formic acid}}{HCOOH} + \underset{\text{Benzyl alcohol}}{ArCH_2OH}$$

ii) **Intramolecular cannizaro reaction** :-

e.g.



$$\underset{\text{Glyoxal}}{H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H} \xrightarrow{OH^{\ominus}} \underset{\text{Glycollate anion}}{H-\overset{OH}{\underset{H}{C}}-C\overset{O}{\underset{O^{\ominus}}{\lessgtr}}}$$