CANNIZZARO REACTION

$$2\,RCHO \xrightarrow[H_3O^{\oplus}]{\text{Conc. base}} RCOOH + RCH_2OH$$

(aldehyde with no α-H) — RCOOH: oxidised; RCH_2OH: Reduced

Aldehydes (having no α-H), undergoing cannizzaro Rxn:-

$PhCHO$, R_3CCHO,  etc.

If having α-H then → Aldol condensation (much faster)

example of cannizzaro rxn:-

$$2\,PhCHO \xrightarrow[2.\ H_3O^{\oplus}]{1.\ \text{Conc. NaOH}} PhCOOH + PhCH_2OH$$

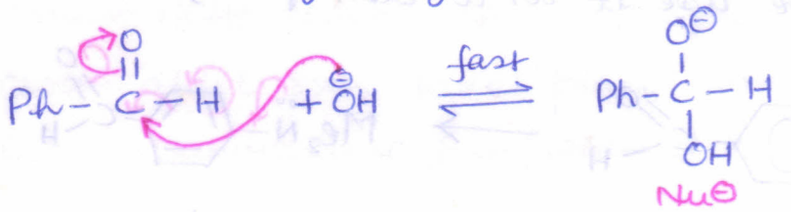
Benzaldehyde — Benzoic acid (oxidised) + Benzyl alcohol (Reduced)

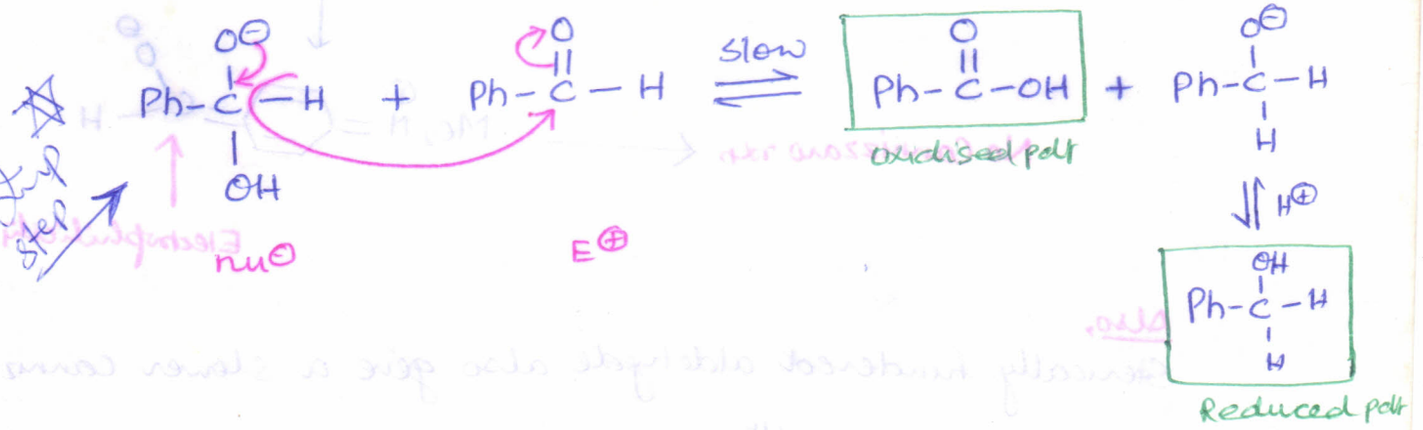
disproportion

mechanism

→ Involve intermolecular **HYDRIDE TRANSFER**

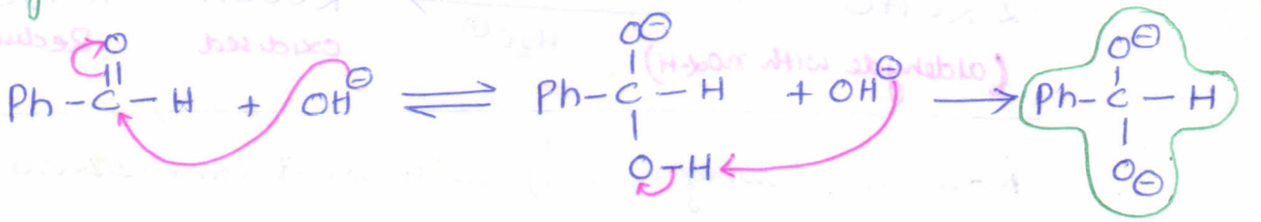
: Confirmed by using D_2O as solvent → no deutoriated pdt found



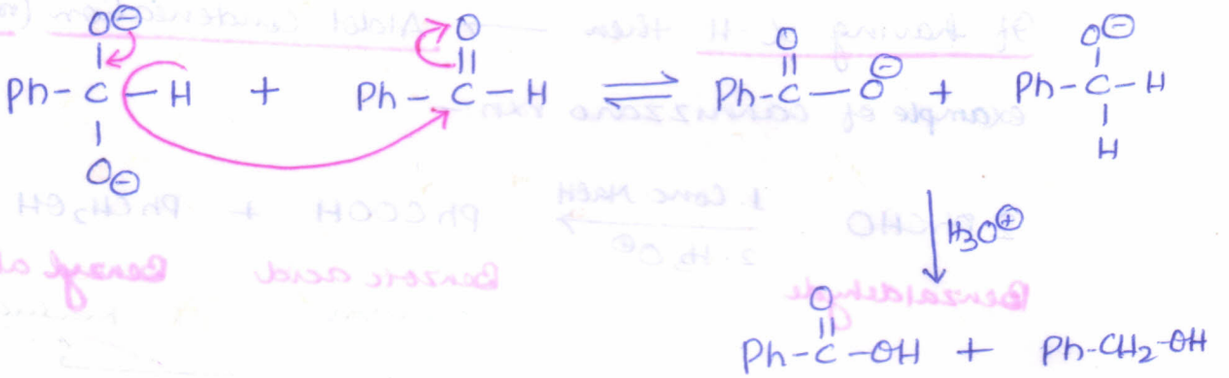


$$\text{Rate} = K[PhCHO]^2[OH^-] : \text{3rd order}$$

When more stronger bases in higher concentration is used, dianion of the aldehyde is formed which is a much better hydride donar than the monoanion :-

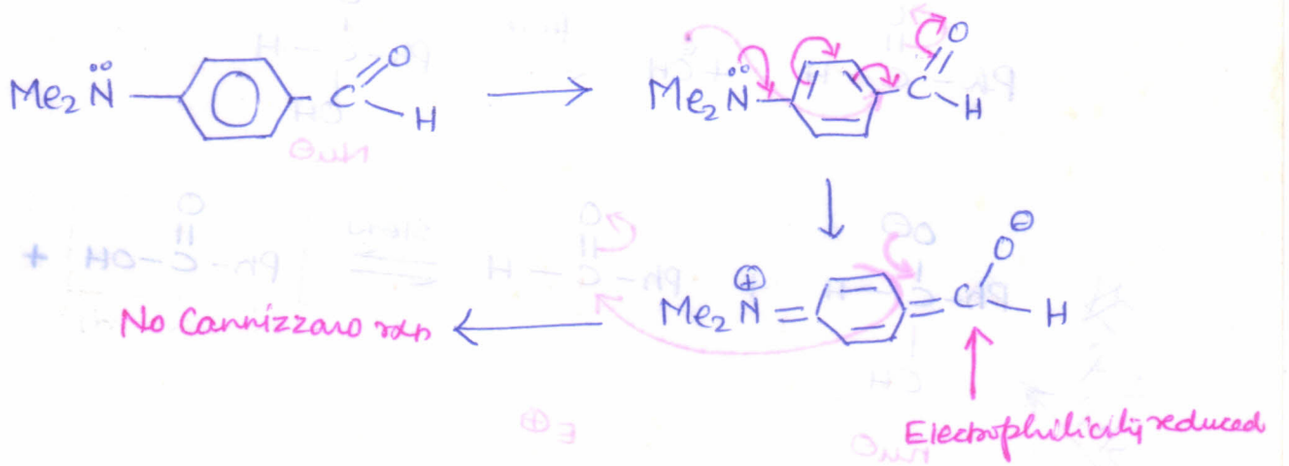


dianion
Better $H^{\ominus}$ donar

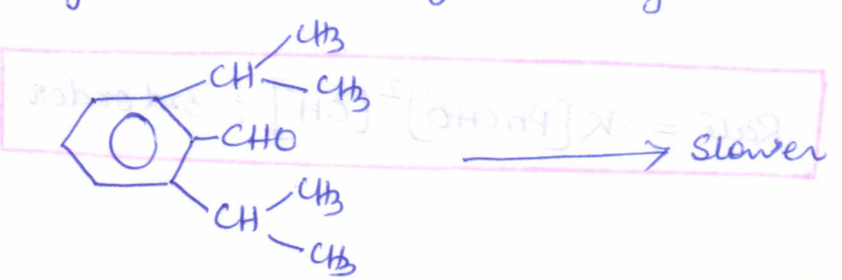


$$\text{Rate} = K[PhCHO]^2[OH^{\ominus}]^2 \Rightarrow \text{4th order}$$

Factors which reduce the electrophilicity of carbonyl centre (as we use it as a electrophile) slower the rate of rxn.



Also,
Sterically hindered aldehyde also give a slower cannizzaro rxn.



Crossed Cannizzaro Rxn

Rxn between two different aldehydes.

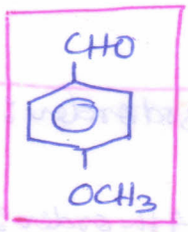
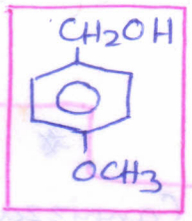
Imp → when formaldehyde undergo cannizzaro rxn with other aldehyde,

$$HCHO \xrightarrow{\text{Oxidised}} HCOOH$$
$$\text{other aldehyde} \xrightarrow{\text{Reduced}} \text{Alcohol}$$

Reason, ∵ Nucleophilic attack on carbonyl centre of HCHO occurs much easily than other aldehyde (due to electronic and steric effect)

example:-

- $PhCHO + HCHO \xrightarrow[H_3O^{\oplus}]{\text{Conc. NaOH}} \underset{\text{Reduced}}{PhCH_2OH} + \underset{\text{Oxidised}}{H\text{-}COOH}$

-  + $HCHO \xrightarrow[H_3O^{\oplus}]{NaOH}$  + $H\text{-}COOH$ (Oxidised)

  (Reduced)

- When HCHO reacts with aldehyde having one α-H, then cross aldol rxn takes place which is followed by cross-cannizzaro Rxn (when α-H absent)

$$\underset{\text{one } \alpha\text{-H}}{(CH_3)_2CH\text{-}CHO} + HCHO \xrightarrow[\text{Aldol rxn}]{\text{Crossed}} \underset{\text{no } \alpha\text{-H}}{(CH_3)_2C(CH_2OH)(CHO)}$$

($Nu^{\ominus}$ / $E^{\oplus}$)

Suitable for can. rxn

Aldehyde having no α-H get oxidised by $OH^{\ominus}$ attacked in 1st step

$$(CH_3)_2C(CH_2OH)(CHO) + HCHO \xrightarrow[\text{cannizzaro rxn}]{\text{Crossed } (OH^{\ominus})} \underset{\text{Reduced}}{(CH_3)_2C(CH_2OH)(CH_2OH)} + \underset{\text{Oxidised}}{HCOOH}$$

note: If there are two α-Hs in an aldehyde then there will be two times aldol rxn, followed by cannizaro reaction (solve question no-1,2)

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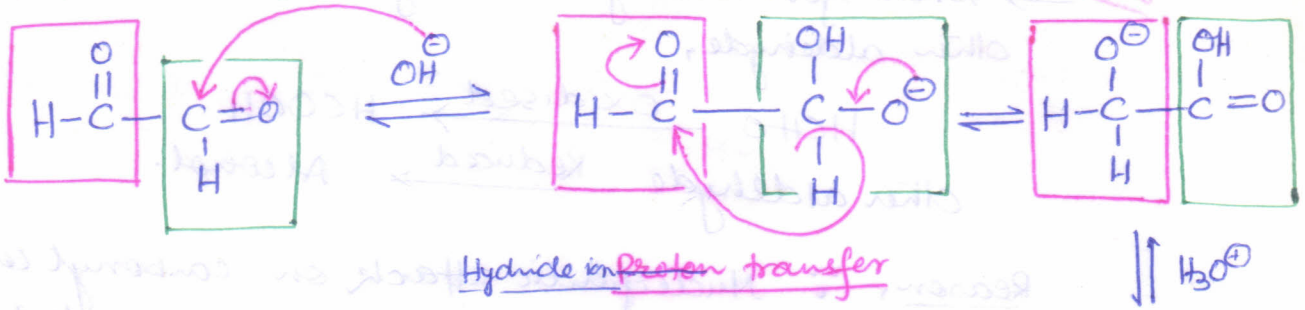
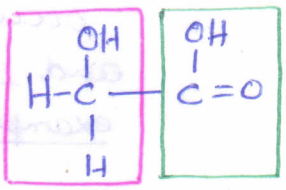
Intramolecular Cannizzaro Rxn :-

Suitable dialdehyde and α-keto aldehyde undergo intramolecular Cannizaro Rxn :-





$$\text{Rate} = K\begin{bmatrix}\text{CHO}\\ \text{CHO}\end{bmatrix}[OH^{\ominus}] : \text{2nd order}$$

Rate of different type of Cannizzaro rxn :-

- ✲ Normal Cannizzaro rxn → 3rd order : $K[PhCHO]^2[OH^-]$
- ✲ Cannizzaro Rxn in strong and conc. basic medium → 4th order : $K[PhCHO]^2[OH^-]^2$
- ✲ Intramolecular Cannizzaro rxn → 2nd order : $K\begin{bmatrix}\text{CHO}\\ \text{CHO}\end{bmatrix}[OH^-]$

Questions

1) $CH_3CH_2CHO + 3HCHO \xrightarrow[H_3O^{\oplus}]{NaOH}$

(2 for crossed aldol, one for cannizaro)

2) $CH_3CHO + 4HCHO \xrightarrow[H_3O^{\oplus}]{KOH}$

3) $2\ \begin{matrix}\text{CHO}\\ |\\ \text{COOH}\end{matrix} \xrightarrow[\Delta]{NaOH}$

4) $Ph-\underset{\underset{O}{\|}}{C}-CHO \xrightarrow{OH^{\ominus}}$