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Lecture 18

(2) Cannizaro's reaction:

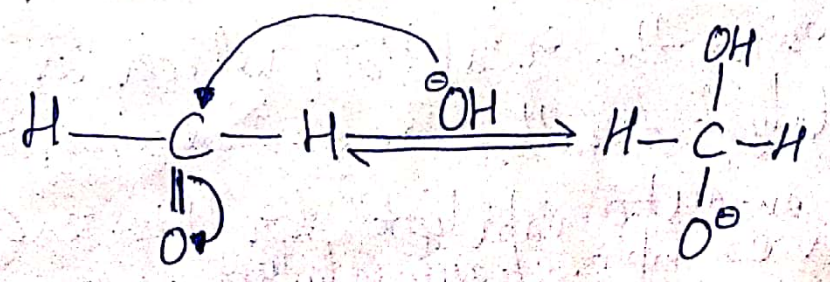
Those aldehydes which do not contain α-H atom give this reaction, with Conc. NaOH or KOH; Products are salt of Carboxylic acid + alcohol.

In this reaction one molecule of Carbony Compounds is oxidised to acid, while other is reduced to alcohol, such type of reactions are called disproportionation reaction.

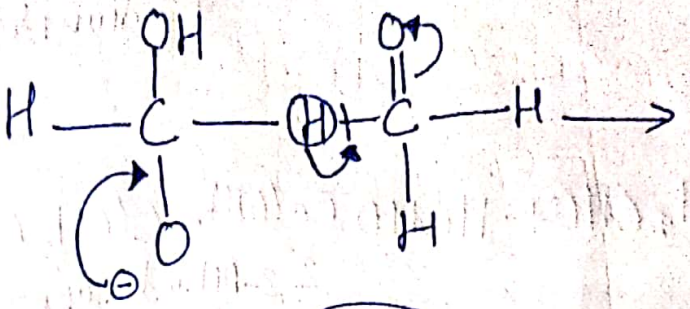
$$HCHO + HCHO \xrightarrow[NaOH]{Conc} HCOONa + CH_3OH$$

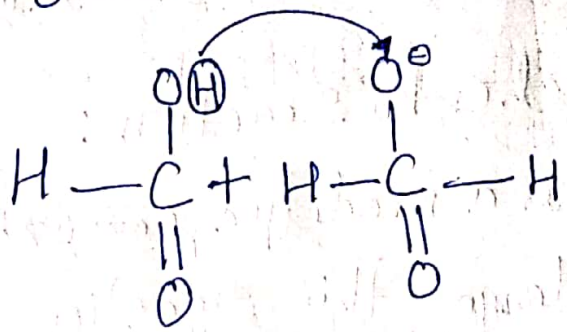
Mechanism: (Cannizaro reaction)

(a) Rapid reversible addition of $\overline{OH}$ to one molecule of HCHO.



(b) Transfer of hydride ion $\overset{\ominus}{H}$ to one molecule of HCHO.

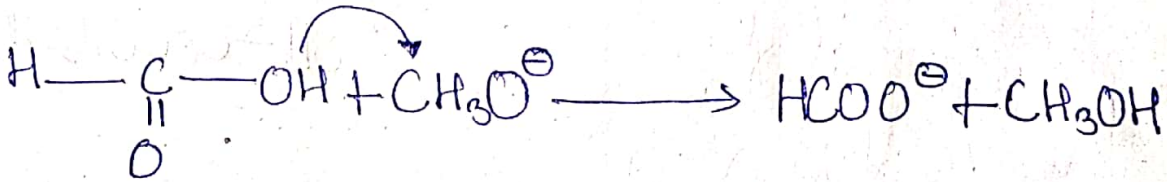




Formic acid — Methoxide ion

↓ Proton exchange

(c) Proton exchange



$$HCOO^{\ominus} + Na^{\oplus} \longrightarrow HCOONa$$

When molecules are same → Simple Cannizzaro reaction

Two different molecules → Mixed Cannizzaro reaction

In mixed or crossed Cannizzaro reaction more reactive aldehyde is oxidised and less reactive aldehyde is reduced.

$HCHO + C_6H_5CHO \xrightarrow{NaOH} HCOONa + C_6H_5CH_2OH$

Oxidized — Reduced

(Sodium formate — (Benzyl alcohol)

Ex: $CH_3CHO + HCHO \xrightarrow{Ca(OH)_2} C(CH_2OH)_4 + (HCOO)_2Ca$ explain mechanism?

2, 2-Dihydroxy methyl-1, 3-Propane diol. (Penta erythritol)

(3) Tischenko reaction:

It is a modified Cannizzaro reaction. All aldehydes undergo this reaction in presence of $(C_2H_5O)_3Al$ to form ester.

$$2RCHO \xrightarrow[\Delta]{(R'O)_3Al} RCH_2-O-\overset{O}{\overset{\|}{C}}-R$$

Ester

Example: $CH_3CHO + CH_3CHO \xrightarrow{(C_2H_5O)_3Al} \underbrace{CH_3COOH + CH_3CH_2OH}_{\text{Esterification}}$

$CH_3-COOCH_2CH_3$ (Ethyl acetate)