Subject : Chemistry.

Class : B.Sc. Part II (Hons.)

Paper : III C, Gr. A. Organic Chemistry.

Topic : Name Reaction and Mechanism

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Chemistry (Hons.)
B.Sc. Part. II (Organic chemistry)
Paper III "C"

Cannizzaro Reaction

Aldehydes not containing an α-hydrogen atom, when treated with conc. alkali solution undergo disproportionation i.e., self oxidation-reduction. As a result, one molecule of the aldehyde is reduced to the corresponding alcohol and the second one is oxidised to the corresponding carboxylic acid. This reaction is called Cannizzaro reaction.

Examples:

$$2\ H-\overset{O}{\overset{\|}{C}}-H + NaOH \longrightarrow CH_3-OH + H-\overset{O}{\overset{\|}{C}}-ONa$$

Formaldehyde (50%) — Methyl alcohol — Sod. formate

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

Benzaldehyde (50%) — Benzyl alcohol — Sod. Benzoate

Mechanism:

Rapid addition of $\overset{\ominus}{OH}$ to one molecule of aldehyde results in the formation of a hydroxy alkoxide ion which like aluminium-isopropoxide act as a hydride-ion donor to the second molecule of aldehyde. In the final step of the reaction, the acid and the alkoxide ion exchange proton for reasons of stability.

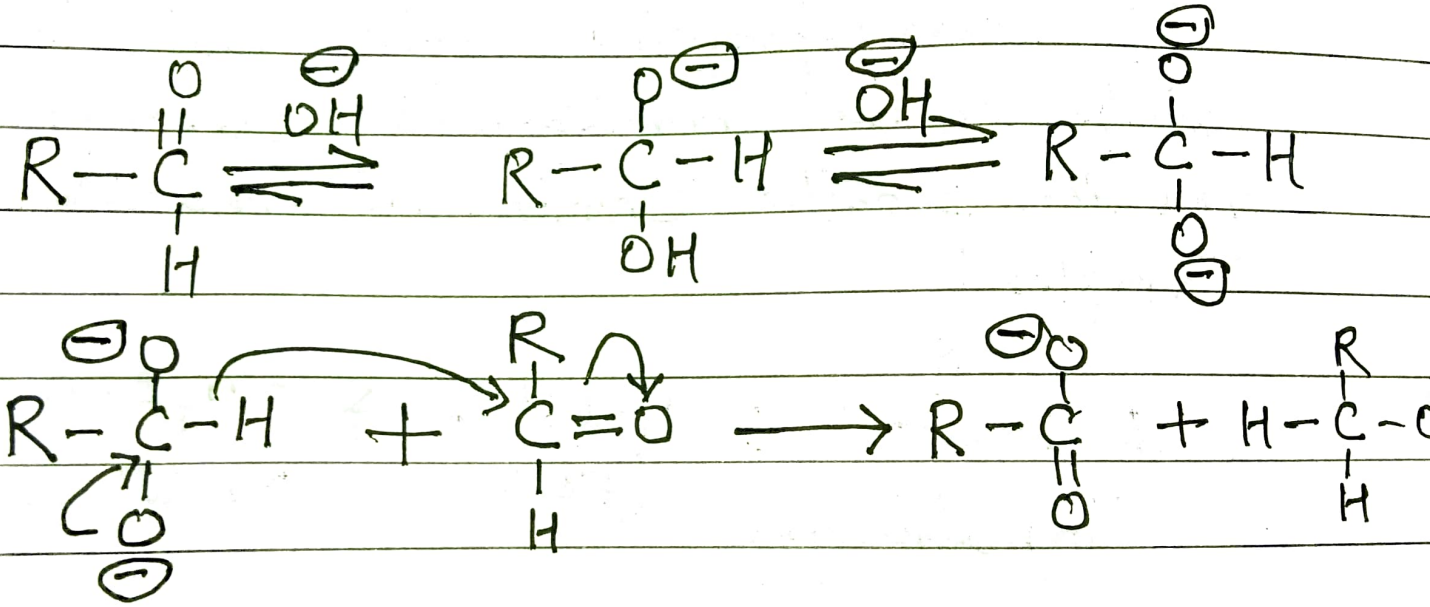
$$C_6H_5-\overset{O}{\overset{\|}{C}}-H + \overset{\ominus}{OH} \rightleftharpoons C_6H_5-\overset{\ominus O}{\underset{H}{C}}-OH$$

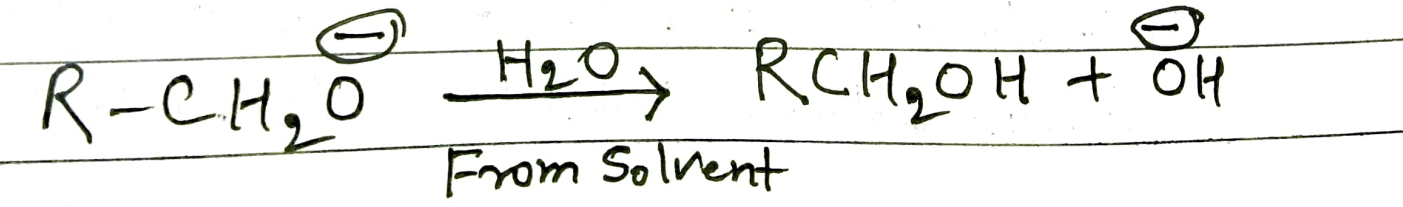
$$C_6H_5-\overset{\ominus O}{\underset{H}{C}}-OH + \overset{O}{\overset{\|}{C}}-C_6H_5 \xrightarrow{\text{Slow}}$$

$$C_6H_5-\overset{O}{\overset{\|}{C}}-OH + H-\overset{\ominus O}{\underset{H}{C}}-C_6H_5 \xrightarrow[(\text{fast})]{\text{proton exchange}}$$

$$C_6H_5-CH_2-OH + C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O} \leftrightarrow C_6H_5-\overset{\ominus O}{\underset{}{C}}=O$$

In the presence of a very strong concentration of alkali, aldehyde first forms a doubly charged anion from which a hydride anion is transferred to the second molecule of the aldehyde to form acid and an alkoxide ion. Subsequently, the alkoxide ion acquires a proton from the solvent.





$$R-CH_2O^{\ominus} \xrightarrow{H_2O} RCH_2OH + OH^{\ominus}$$

From Solvent