▶ Video explanation (YouTube Short)

The Cannizzaro Reaction

Two identical aldehyde molecules go in. One comes out as a carboxylic acid salt, the other as an alcohol. One molecule is oxidised and the other is reduced, in the same reaction.

1. Definition and condition

Aldehydes that have **no α-hydrogen** (for example methanal HCHO and benzaldehyde C_6H_5CHO), when heated with **concentrated** NaOH or KOH, undergo self oxidation and reduction (**disproportionation**). One molecule is oxidised to a carboxylic acid salt and the other is reduced to an alcohol.

$2\,C_6H_5CHO + NaOH\ (conc.) \rightarrow C_6H_5COONa + C_6H_5CH_2OH$

$2\,HCHO + NaOH\ (conc.) \rightarrow HCOONa + CH_3OH$

- **α-hydrogen:** a hydrogen on the carbon next to the C=O group. In benzaldehyde that carbon is a ring carbon with no H; HCHO has no such carbon at all.
- With an α-hydrogen and dilute base, aldehydes give **aldol** instead.
- Benzoic acid itself is obtained only after the sodium benzoate is acidified.

2. Mechanism (three steps)

Step	What happens
1. Nucleophilic addition	OH^- attacks the carbonyl carbon of molecule A. The C=O π bond moves to O: a tetrahedral intermediate with O^-, OH and H on one carbon.
2. Hydride transfer (key step)	The O^- re-forms C=O, and the C–H bond's electron pair carries H^- **directly** to the carbonyl carbon of molecule B. A becomes benzoic acid; B becomes a benzyl alkoxide ion.
3. Proton transfer	The acid gives its proton to the alkoxide: **benzoate ion** + **benzyl alcohol**.

Careful: the hydride is never free in the solution. It passes straight from one molecule to the other.

3. Why it is oxidation and reduction

Oxidation number of the carbonyl carbon, counting bonds: each bond to O is +1, each bond to H is −1, a bond to C is 0.

Carbon	Bonds	Oxidation number
C of C_6H_5CHO	C=O, C–H, C–C	+1
C of $C_6H_5COO^-$	C=O, C–O^-, C–C	**+3 (oxidised)**

C of $C_6H_5CH_2OH$	C–O, 2 C–H, C–C	**−1 (reduced)**

Solved example

Q. Which of these give the Cannizzaro reaction: HCHO, CH_3CHO, C_6H_5CHO, $(CH_3)_3CCHO$? Write the products for one of them.
A. HCHO, C_6H_5CHO and $(CH_3)_3CCHO$ have no α-hydrogen, so they do. CH_3CHO has three α-hydrogens and gives aldol. For HCHO: 2 HCHO + NaOH (conc.) → HCOONa + CH_3OH.

Key takeaways

- No α-hydrogen + concentrated alkali → Cannizzaro.
- Two identical molecules, two fates: one oxidised (carboxylate), one reduced (alcohol).
- The key step is a direct hydride transfer.
- It is a disproportionation reaction.

Practice questions

1. (MCQ) Which aldehyde does not give the Cannizzaro reaction? (a) HCHO (b) C_6H_5CHO (c) CH_3CHO (d) $(CH_3)_3CCHO$
2. (MCQ) In the Cannizzaro reaction of benzaldehyde, the reduced product is: (a) benzoic acid (b) benzyl alcohol (c) sodium benzoate (d) benzene
3. (Very short) Name the condition on the aldehyde for the Cannizzaro reaction.
4. (Very short) What is the key step that links the two molecules?
5. (Short) Write the Cannizzaro reaction of methanal and name the products.
6. (Short) Why is the Cannizzaro reaction called a disproportionation reaction?
7. (Application) An aldehyde $C_5H_{10}O$ gives the Cannizzaro reaction. Identify it.
8. (Numerical) Find the oxidation number of the carbonyl carbon in HCHO and in $HCOO^-$.

Answer key

1. (c) CH_3CHO has α-hydrogens.
2. (b) Benzyl alcohol.
3. It must have no α-hydrogen (and the alkali must be concentrated).
4. A direct hydride (H^-) transfer from the tetrahedral intermediate to the second molecule.
5. 2 HCHO + NaOH (conc.) → HCOONa + CH_3OH: sodium methanoate and methanol.
6. The same compound is oxidised (carbon +1 → +3) and reduced (carbon +1 → −1) in one reaction.
7. 2,2-Dimethylpropanal, $(CH_3)_3CCHO$: its α-carbon carries no hydrogen.
8. HCHO: C=O (+2) and 2 C–H (−2): 0. $HCOO^-$: C=O, C–O^- (+3) and C–H (−1): +2.

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