CHAPTER III

CHEMISTRY OF SUCROSE HYDROGENOLYSIS REACTION
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During hydrogenolysis, splitting of a chemical bond is accomplished using hydrogen. In general, the process can be represented by the following reaction:

\[ XY + H_2 \rightarrow XH + YH \]

Where X is usually a carbon atom and Y may be a carbon, nitrogen, oxygen, sulphur or a halogen atom. The splitting may be assisted by a heterogeneous catalyst. Several stages exist, during interaction of the catalyst with an organic compound. Initially, both in the presence or absence of hydrogen as a reactant, radicals are formed by hydrogen atom removal, which are held to the catalyst surface by multipoint adsorption. This occurrence requires a minimum temperature. At higher temperatures and in the presence of hydrogen, the carbon-carbon bonds rupture to form lower molecular weight products. Hydrogenolysis in sucrose molecule results in the formation of various polyalcohols and monosaccharides at suitable temperature and pressure.

Sucrose is a disaccharide in which the aldehydic group of glucose and the ketonic group of fructose are involved in glycosidic bonding thus making the molecule non-reducing. The presence of fructose ring facilitates the hydrogenolysis of sucrose at milder conditions [73].
The ring configuration of the constituent D-glucose & D-fructose residues in sucrose molecule and the type of glycosidic linkage (α or β) involved in each monosaccharide residue shows that glucose exist in sucrose as α-D-glucopyranose and fructose exists as β-D-fructofuranose form. Therefore the conformational structure of sucrose shows that it is \( \alpha-D\)-glucopyranosyl \( \beta-D\)-fructofuranoside.

\[ \alpha-D\text{-Glucopyranosyl } \beta-D\text{-Fructofuranoside} \]

(Configuration str. of Sucrose)

Thus in the presence of a heterogenous catalyst and a suitable additive, sucrose may either give glucose and fructose by splitting at ether linkage or may break at other bonds simultaneously to produce glycerol and other glycols. Fig. 3.1 shows various possible routes of products formation during hydrogenolysis of sucrose.

Various probable rupture sites of a sucrose molecule are shown below by hatched lines -
Fig. 3.1. Various Possible Routes of Products Formation During Hydrogenolysis of Sucrose.
The rupture at ether linkage may produce glucose and fructose molecules via Route R_1 (Fig. 3.1)

Glucose

Fructose

Breaking at ether linkage with simultaneous hydrogenolysis may lead to the formation of sorbitol and mannitol via Route R_2 (Fig. 3.1).

Sorbitol

Mannitol

Splitting at C_1-C_2 or C_5-C_6 bond, along with rupture at ether linkage, may result the formation of 2 moles of xylitol and methanol via Route R_3 (Fig. 3.1).

Xylitol

Methanol
Similarly route $R_4$ may produce either 2 moles of erythritol and ethylene glycol by splitting at $C_2-C_3$ bond or 6 moles of ethylene glycol by simultaneous breaking at $C_2-C_3$ and $C_4-C_5$ bonds. (Fig. 3.1)

![Chemical structures: Ethylene glycol and Erythritol]

Erythritol may further yield 2,3 butane diol by eliminating a water molecule, following the route $R_5$ (Figs. 3.1 and 3.2).

![Chemical structures: Erythritol to 2,3 Butane diol]

Route 6 indicates the rupture of $C_3-C_4$ bond and ether linkage, resulting 4 moles of glycerol. This breaking may be associated with elimination of water molecule to produce propylene glycol. (Fig. 3.1).

![Chemical structures: Glycerol and Propylene-glycol]
Fig. 3.2. Various Possible Routes of Products Formation During Hydrogenolysis of Glucose and Fructose.
In the present investigation, some additives have been found to promote hydrolysis of sucrose, specifically forming glucose and fructose molecules via Route $R_1$ and $R_2$. These monosaccharides may then hydrogenate or hydrogenolyse to produce other products as shown in fig. 3.2. The hydrogenation would form sorbitol in case of glucose & sorbitol and mannitol in case of fructose via Routes $R_7$, $R_{8A}$ and $R_{8B}$ respectively. Thus the following reaction may be proposed.
It is known[47] that glucose, in presence of an alkali and a hydrogenation catalyst, undergoes (i) hydrogenation to form sorbitol and (ii) hydrogenolysis to produce glycerol and glycols. Hydrogenolysis of glucose is favoured at lower temperatures where as its hydrogenation to sorbitol, predominates at higher temperatures. Sorbitol thus formed, may further hydrogenolyse to produce glycerol and glycols.

Length and DuPuis [11] proposed the following
reaction schemes for the formation of glycerol and glycols from glucose via its hydrogenation to sorbitol. Sorbitol may thus be obtained through reaction scheme (3.2) and then may break at C_3-C_4 bond to produce glycerol via route R_{15} (Figs. 3.1 and 3.2).

\[
\text{H H H H H H} \quad \text{Catalyst, additive} \quad 2 \begin{bmatrix} 
\text{H H H} \\
\text{O O O O} \\
\text{H H H H}
\end{bmatrix} \rightarrow \begin{bmatrix} 
\text{H H H} \\
\text{O O O} \\
\text{H H H}
\end{bmatrix}
\]

Sorbitol

Cleavage at C_3-C_4 bond

Simultaneous formation of propylene glycol from glycerol has also been proposed via route R_{17} (Figs. 3.1 and 3.2) as per following scheme.

\[
\text{H H H} \quad \text{Catalyst, additive} \quad \text{H C C C C H} + \text{H}_2 \rightarrow \begin{bmatrix} 
\text{H H H} \\
\text{O O O} \\
\text{H H H}
\end{bmatrix} \rightarrow \begin{bmatrix} 
\text{H H H} \\
\text{O O H} \\
\text{H H}
\end{bmatrix}
\]

Glycerol

Propylene-glycol

Formation of propylene glycol may also take place, directly from sorbitol via route R_{18} (Figs. 3.1 & 3.2) as
Vasyumina [36, 37] has proposed formation of following chelate by certain metal hydroxides at C$_3$–C$_4$, the weakest bonds of sorbitol.

This chelate formation further weakens this bond and presence of a catalyst induces its cleavage to yield glycerol and propylene-glycol.
glycol as per reaction schemes (3.4) and (3.7) respectively. The cleavage at C$_4$-C$_5$ bond of sorbitol would result in the formation of ethylene and erythritol via route $R_{20}$ (Figs. 3.1 & 3.2) as depicted in reaction scheme (3.8).

\[
\text{Sorbitol} + H_2 \xrightarrow{\text{Catalyst, additive}} \text{Ethylene glycol} + \text{Erythritol} \quad (3.8)
\]

If only above reaction is present, it would yield ethylene-glycol and erythritol in equimolar proportion. However appreciable amounts of ethylene glycol was found by Fadeeva[47] with negligible contents of erythritol in the reaction products. Therefore either another route exists for the formation of ethylene glycol or it is formed by further decomposition of erythritol at C$_2$-C$_3$ bonds as indicated by route $R_{22}$ in figures 3.1 & 3.2.

\[
\text{Erythritol} + H_2 \xrightarrow{\text{Catalyst, additive}} 2 \left[ \begin{array}{c} \text{Ethylene-glycol} \\ \text{H-C-C-H} \end{array} \right] \quad (3.9)
\]
There is yet another possibility of ethylene glycol formation by simultaneous cleavage of C₂-C₃ and C₄-C₅ bonds in sorbitol molecule.

\[
\begin{align*}
\text{H} & \text{H} \text{H} \text{H} \text{H} \text{H} \\
\text{H-C-C-C-C-C-H} & + \text{H}_2 \\
\text{Catalyst,} & \text{ additive} \\
\rightarrow & \text{3} \\
\text{H} & \text{H} \\
\text{H-C-C-H} & \\
\text{H} & \text{H} \\
\text{Ethylene-glycol}
\end{align*}
\]

Sorbitol may also yield xylitol and methanol by cleavage at C₁-C₂ bond via route R₂₃ (Figs. 3.1 & 3.2) as shown in reaction scheme 3.11.

\[
\begin{align*}
\text{H} & \text{H} \text{H} \text{H} \text{H} \text{H} \\
\text{H-C-C-C-C-C-H} & + \text{H}_2 \\
\text{Catalyst,} & \text{ additive} \\
\rightarrow & \text{H-C-C-C-C-H} + \text{H-C-H} \\
\text{Sorbitol} & \text{(Cleavage at C₁-C₂ bond)} \\
\text{Xylitol} & \text{Methanol}
\end{align*}
\]

Similarly Mannitol can also react to produce various products via the routes indicated in Figs. 3.1 & 3.2. Glycols and polyols, other than sorbitol and mannitol may also be obtained by direct hydrogenolysis of glucose and fructose as shown in Fig. 3.2.

Thus, several parallel and consecutive reactions are present during sucrose hydrogenolysis, making it a very complex
phenomenon. These reactions resulting in the formation of monosaccharides and polyhydric alcohols, can be summarised as follows:

1. Hydrolysis of sucrose into glucose and fructose.
2. Hydrolysis of sucrose with simultaneous hydrogenation of α-D-glucopyranose and β-D-fructofuranose moieties into sorbitol and mannitol.
3. Hydrogenolysis of sucrose into glycerol and glycols.
4. Hydrogenation of glucose and fructose into sorbitol and mannitol.
5. Hydrogenolysis of glucose and fructose into glycerol & glycols.
6. Hydrogenolysis of sorbitol and mannitol giving various lower molecular wt. polyols.
7. Hydrogenolysis of polyols, other than sorbitol and mannitol, giving products with still lower molecular wt.

Among the above discussed products glycerol, ethylene glycol, propylene glycol, sorbitol, glucose, fructose and the unreacted sucrose have been identified. Formation of certain other components were indicated by some unidentified spots on TLC plate. On varying the additives and their concentrations, the reaction mechanism may alter, thus affecting the product distribution.

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