**Hydrogenolysis** is a chemical reaction whereby a carbon–carbon or carbon–heteroatom single bond is cleaved or undergoes "lysis" by hydrogen.[1] The heteroatom may vary, but it usually is oxygen, nitrogen, or sulfur. A related reaction is **hydrogenation**, where hydrogen is added to the molecule, without cleaving bonds. Usually hydrogenolysis is conducted catalytically using hydrogen gas.

### History

The term "hydrogenolysis" was coined by Carleton Ellis in reference to hydrogenolysis of carbon–carbon bonds.[1][2] Earlier, Sabatier had already observed the hydrogenolysis of benzyl alcohol to toluene,[3] and as early as 1906, Padoa and Ponti had observed the hydrogenolysis of furfuryl alcohol.[4] Adkins and Connors were the first to call the carbon–oxygen bond cleavage "hydrogenolysis".[1]

### Petrochemical industry

In petroleum refineries, catalytic hydrogenolysis of feedstocks is conducted on a large scale to remove sulfur from feedstocks, releasing gaseous hydrogen sulfide (H₂S). The hydrogen sulfide is subsequently recovered in an amine treater and finally converted to elemental sulfur in a Claus process unit. In those industries, desulfurization process units are often referred to as hydrodesulfurizers (HDS) or hydrotreaters (HDT). Catalysts are based on molybdenum sulfide containing smaller amounts of cobalt or nickel. Hydrogenolysis is accompanied by hydrogenation.[5]

Another hydrogenolysis reaction of commercial importance is the hydrogenolysis of esters into alcohols by catalysts such as copper chromite.

### In the laboratory

In the laboratory, hydrogenolysis is used in organic synthesis. Debenzylation is most common and involves the cleavage of benzyl ethers:[6]

\[ \text{ROCH}_2\text{C}_6\text{H}_5 + \text{H}_2 \rightarrow \text{ROH} + \text{CH}_3\text{C}_6\text{H}_5 \]

Thioketals undergo hydrogenolysis using Raney nickel in the Mozingo reduction.

Laboratory hydrogenolysis is operationally similar to hydrogenation, and may be accomplished at atmospheric pressure by stirring the reaction mixture under a slight positive pressure of hydrogen gas, having flushed the apparatus with more of this gas. The hydrogen may be provided by attaching a balloon to a needle, filling it from a bottle, and inserting the needle into the reaction flask via a rubber septum. At high pressure, a hydrogenation autoclave (i.e., a Parr hydrogenator) or similar piece of equipment is required.

### Desulfurization

Raney nickel is used in organic synthesis for desulfurization. For example, thioacetals will be reduced to hydrocarbons in
the last step of the Mozingo reduction:[14][15]

\[
\text{Thioacetal} \xrightarrow{\text{H}_2, \text{Raney Ni}} \text{CH}_2 + \text{H}_2\text{C=CH}_2 + 2 \text{NiS}
\]

Thiols,[16] and sulfides,[17] can be removed from aliphatic, aromatic, or heteroaromatic compounds. Likewise, Raney nickel will remove the sulfur of thiophene to give a saturated alkane.[18]

References

15.
Further Reading

*Master Organic Chemistry*

Raney Nickel