

Chemical Compound: Alcohols - General Formula and Functional Group

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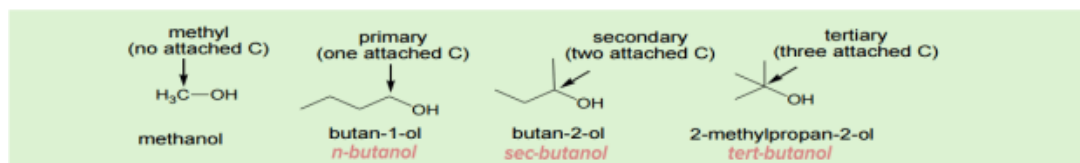
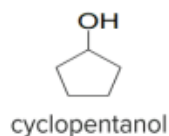
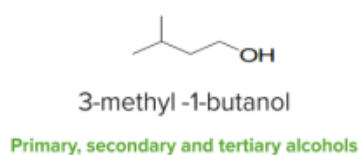
Alcohols are functional groups that are characterized by one or more -OH groups attached to a carbon of hydrocarbon chain. They are organic derivatives of water where hydrogen ion is replaced by an alkyl group. They don't leave their molecular structure on their own. They have high boiling points. They are polar in nature with asymmetrical distribution of charge between oxygen and hydrogen atoms. At room temperature, alcohols are colorless liquids or solids. Ethanol and methanol are common types. They are used in beverages, antifreeze, fuels, and preservatives and for sterilization. Selected reactions of alcohol will also be discussed; namely the synthesis of haloalkanes from alcohols, acid-catalyzed dehydration, esterification reactions and redox reactions involving alcohols.



Nomenclature and Classification

General formula: ROH

Nomenclature: The final -e of the alkane is replaced with -ol.



Alcohol is **an organic compound containing a hydroxyl (R-OH) group**. It may be classified as **primary (1°), secondary (2°) and tertiary (3°)** based on where the hydroxyl group is attached. Primary alcohols are alcohols where the hydroxyl carbon is bound to one other carbon atom. In secondary alcohols, the hydroxyl carbon is attached to two other carbon atoms, and in tertiary alcohols, they are attached to three other carbon atoms. **Below are the general structures of these three types of alcohol:**

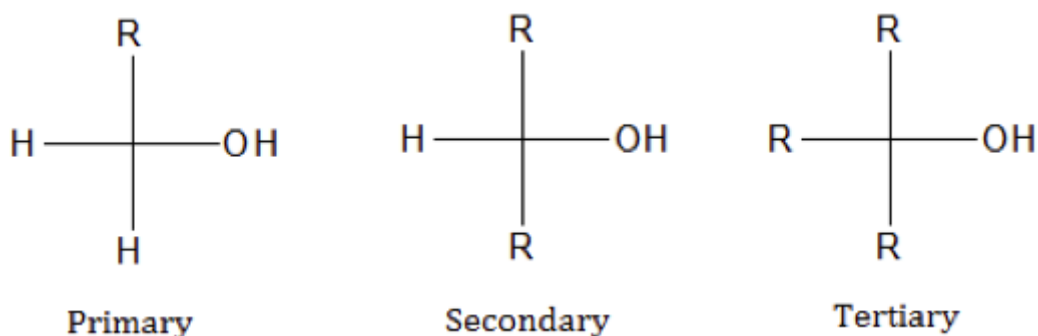
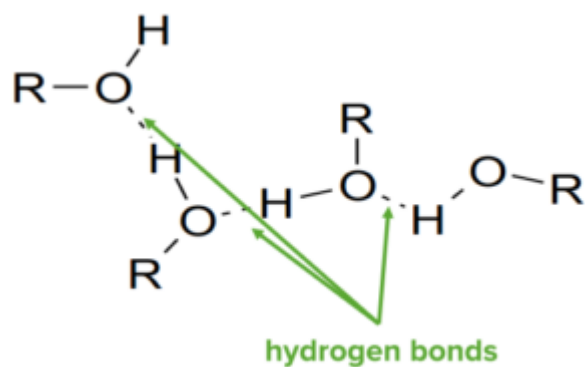


Figure: "Classes of Alcohols." by Mark Xavier Bailon.

Compared to an alkane, alcohol has a much **higher boiling point than the alkane of similar molecular weights**. This is because of the different governing intermolecular forces of attraction (IMF) for the two compounds. For alkane, the major IMF present is only the London Dispersion Forces.

This is because of the compound's non-polar nature. However, for alcohol, the -OH group helped the compound exhibit much stronger IMF in the form of hydrogen bonding.

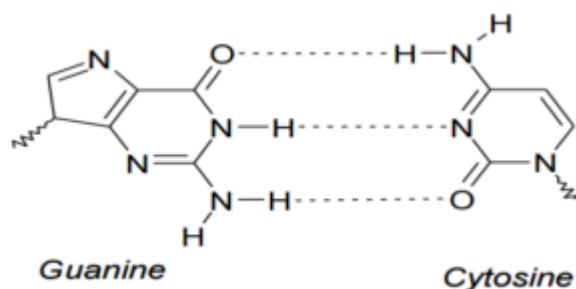
Hydrogen Bonds (H-bonds) form when a Hydrogen atom binds to the small, highly electronegative atoms, such as nitrogen, oxygen, and fluorine, and forms an electrostatic attraction to another nearby highly electronegative atom (F, O, N). Because of the strong interaction between the H atom and the electronegative atom, alcohol molecules are more attracted to each other and have a higher boiling point than alkanes.



Note: A hydrogen bond is a special type of attractive interaction that exists between an electronegative atom and a hydrogen atom bonded to another electronegative atom.

It has only 5–10 % of a covalent bond's strength, but it has a profound effect on the boiling point and solubility of alcohols.

The cells of living things are made up of many different sorts of molecules. Two important classes of molecules are **nucleic acids** and **proteins**. Parts of these very large molecules are involved in hydrogen bonds with other parts of the same molecules. This is very important in establishing the molecules'



structures and properties. The double helix structure of DNA, for example, is mainly due to hydrogen bonding between the base pairs. Two strands of complementary bases are bonded together through the hydrogen bond, which enables replication.

Note: For example, hydrogen bonding plays an important role in determining the three-dimensional secondary structures of proteins.

Hydrogen bonds form between backbone oxygen and amide hydrogen to form more frequently either the α -helix or the β -sheet secondary structure of proteins.

Boiling points (b.p.): more energy is needed to break the hydrogen bonds between molecules, so the b.p. is higher than in an alkane of similar M.W.

nr C	Alkane	b.p. (°C)	Alcohol	b.p. (°C)
1	CH ₄	- 161	CH ₃ OH	64.7
2	CH ₃ CH ₃	- 88	CH ₃ CH ₂ OH	78
3	CH ₃ CH ₂ CH ₃	- 42	CH ₃ (CH ₂) ₂ OH	97
4	CH ₃ (CH ₂) ₂ CH ₃	- 0.5	CH ₃ (CH ₂) ₃ OH	≈ 116
5	CH ₃ (CH ₂) ₃ CH ₃	≈ 35	CH ₃ (CH ₂) ₄ OH	≈ 136

Note it is relatively soluble in water, especially for low M.W. alcohols.

MeOH; EtOH; PrOH-----**water-miscible**

Butanol-----**8 % w/w (8 g/100 g)**

Pentanol-----**2 % w/w (2 g/100 g)**

Preparation of Alkyl Halides from Alcohols

Because of the inherent polarity of alcohol, this organic compound family is considered more reactive than its hydrocarbon counterpart. One of the essential reactions of alcohol is its reaction with a hydrogen halide to produce an alkyl halide and water.



Different types of hydrogen halides have different reactivities for this reaction. The reactivity of hydrogen halides parallels their acidity. This means HI, being the strongest acid, will be the most reactive, and HF, being the weakest acid, will be the least reactive.

Reactivity: HI > HBr > HCl >> HF

The reaction kinetics also depend on the type of alcohol used in the reaction. Different alcohol types also have different reactivities. The reactivity of alcohols with hydrogen halides are shown below.

Methyl (CH₃OH) < Primary (RCH₂OH) < Secondary (R₂CHOH) < Tertiary (R₃COH)

Tertiary alcohols produce high yields in less time than other alcohol types. To increase the rates of reactions for secondary and primary alcohols, the scientist usually performs the reaction at elevated temperatures.

The reaction of alcohol and a hydrogen halide is a substitution reaction. The halogen group replaces the -OH group in the structure. The reaction proceeds through three elementary steps. The first step involves the attachment of the acidic proton to the oxygen atom of the hydroxyl group. This intermediate is highly unstable. Thus, step 2 consists of the removal of a water molecule from the alkyloxonium ion, producing a carbocation intermediate. On the last step, the chloride ion attaches itself to the carbonation, producing the final alkyl halide. As an example, consider the reaction of 2-propanol and HBr at an elevated temperature.

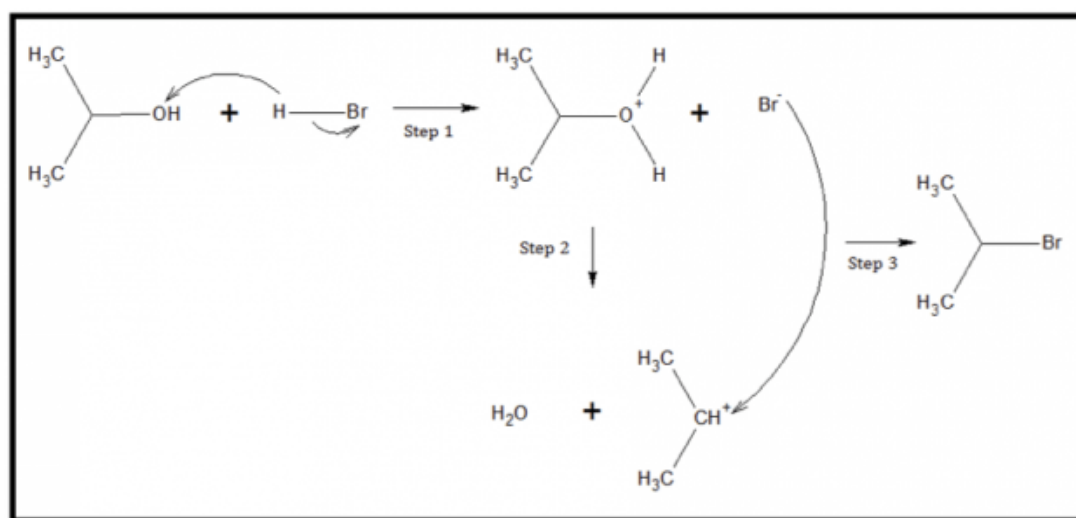


Figure: "Reaction of 2-propanol and HBr to produce 2-bromopropane." by Mark Xavier Bailon.

Elimination of Water

Another important reaction of alcohol is in the production of alkenes. The reaction proceeds once water is eliminated. Except for primary alcohols, reactions, just like in the other alkene preparation method, are regioselective; that is, a mixture of products will form, but one will form in a larger amount. Even though a mixture of products will form, alcohol's dehydration reaction is stereoselective; that is, it favors the production of the most stable stereoisomer.

Alcohol dehydration is catalyzed by strong acids, like H₂SO₄, and heating. The reaction also requires three steps. **Step 1 involves a proton from the acid attaching to the O atom of the -OH group, forming the alkyloxonium ion. Step 2 involves the dehydration, or removal of a water molecule from the alkyloxonium ion, leaving a carbocation intermediate.** The carbocation intermediate then participates as a strong Bronsted acid, donating one H⁺ to a water molecule and regenerating the original proton used up in step 1. Below is the mechanism of an alkene formation through an acid-catalyzed dehydration reaction of 3-propanol.

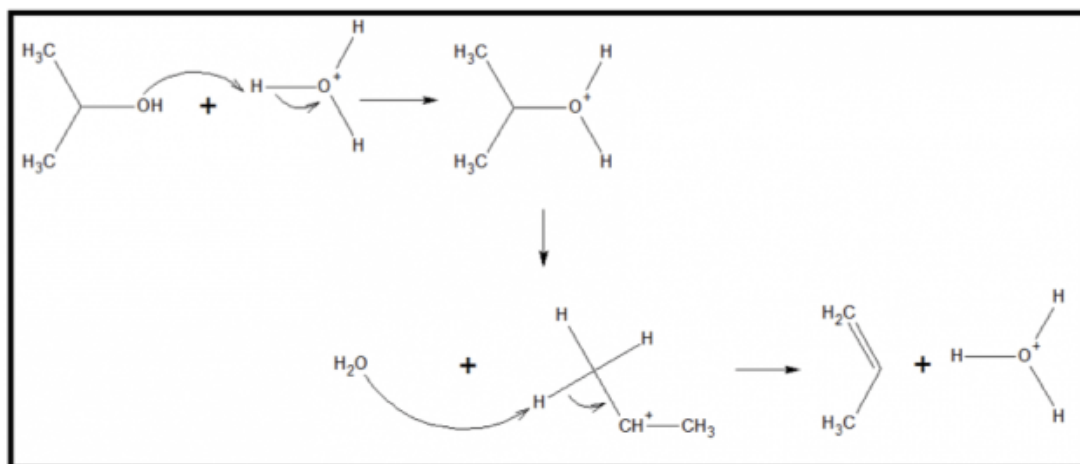
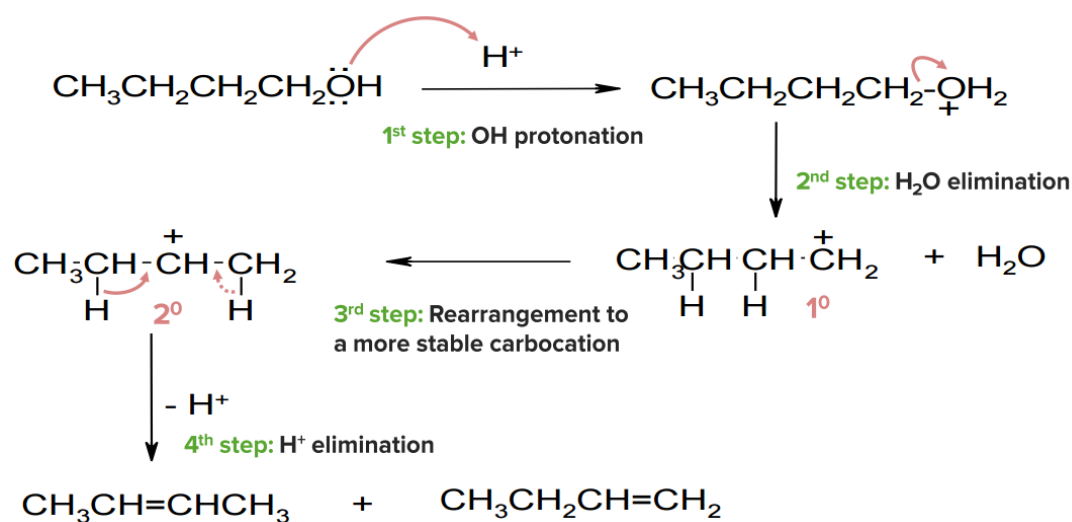


Figure: "Acid-catalyzed dehydration reaction of 2-propanol." by Mark Xavier Bailon.

Mechanism and Rearrangement



Ester Formation

Alcohol is also important in the preparation of esters. Esters are compounds produced by the acid-catalyzed condensation of the alcohol and a carboxylic acid. The general reaction is reversible but favors the products when simple alcohols and carboxylic acids are used. The number of alkyl substituents of alcohol affects its reactivity in an esterification process. The more alkyl substituents, the less reactive it is to esterification for steric reasons.

Reactivity to Esterification:

Methyl (CH₃OH) > Primary (RCH₂OH) > Secondary (R₂CHOH) > Tertiary (R₃COH)

The first step in the esterification process is the protonation of the carbonyl oxygen atom of the carboxylic acid. Because of the interaction between the proton and oxygen, the carbonyl carbon becomes very susceptible to a nucleophilic attack by the oxygen atom of the alcohol. The next step involves a proton transfer from the alcohol group to the -OH of the carboxylic acid. Because of the relative instability of the ion produced, water readily leaves the structure. The last step involves regenerating the proton used up in the first

step. The figure below shows the general mechanism for the reaction.

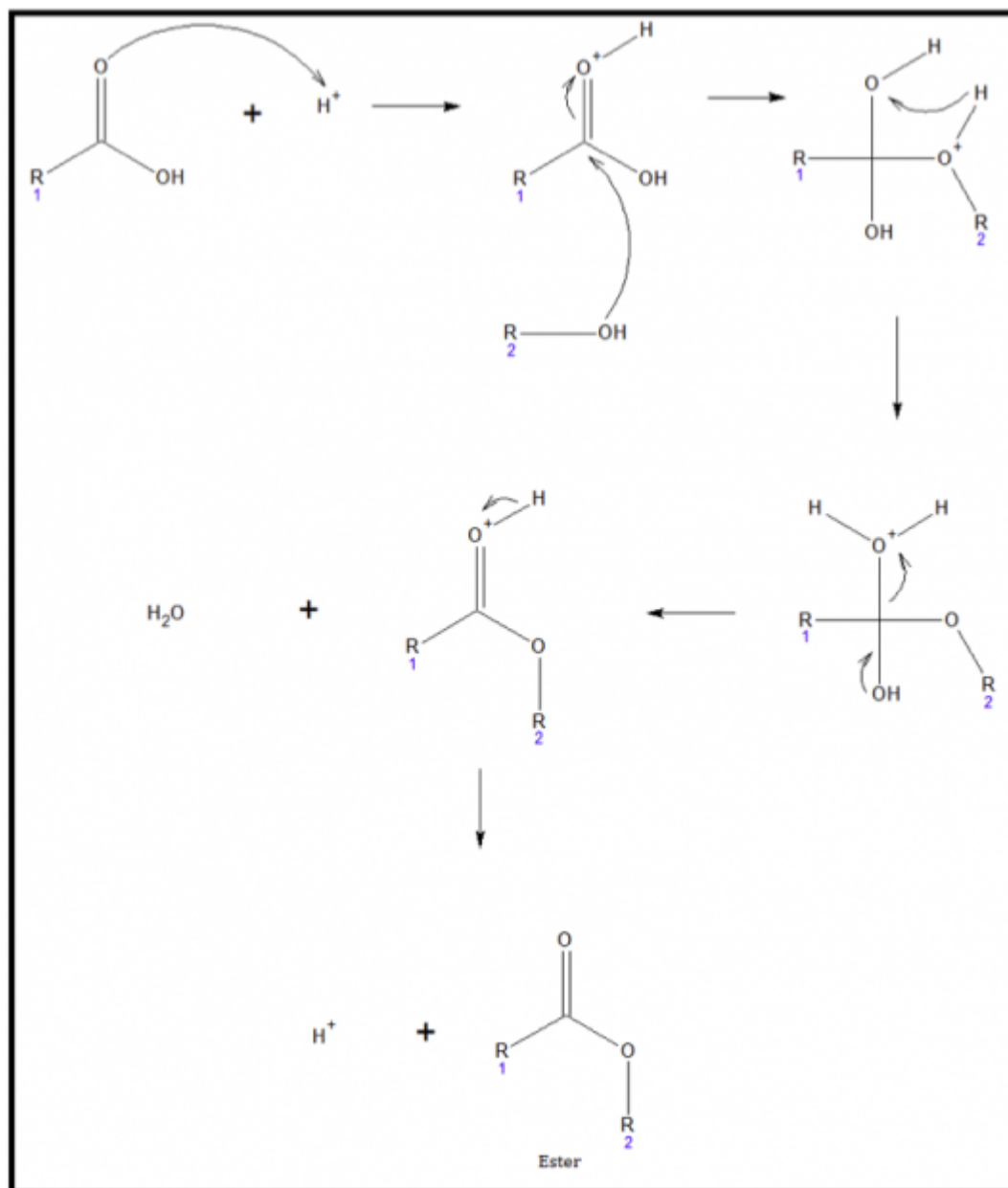


Figure: "Acid-catalyzed esterification." by Mark Xavier Bailon.

Redox Reactions and Enzymes

Alcohols can be converted to a carbonyl compound by reaction with an oxidizing agent. It can be converted into an aldehyde, a ketone, or a carboxylic acid. Primary alcohols may be oxidized to produce either an aldehyde or a carboxylic acid. The usual oxidizing agent for this reaction is **dichromate ($\text{Cr}_2\text{O}_7^{2-}$)**, **pyridinium chlorochromate (PCC - $\text{C}_5\text{H}_5\text{NH}^+ \text{ClCrO}_3^-$)**, **$\text{C}_5\text{H}_5\text{NH}^+$** , and **pyridinium dichromate (PDC - $(\text{C}_5\text{H}_5\text{NH})_2^{2+} \text{Cr}_2\text{O}_7^{2-}$)**. Secondary alcohols are oxidized to ketones using the same set of reagents. Tertiary carbons cannot undergo oxidation since they lack hydrogen on their hydroxyl-bearing carbon.

In biological systems, enzymes can induce oxidation of alcohols and/or the reduction of carbonyl compounds to alcohols. For example, in the liver, ethanol may be metabolized

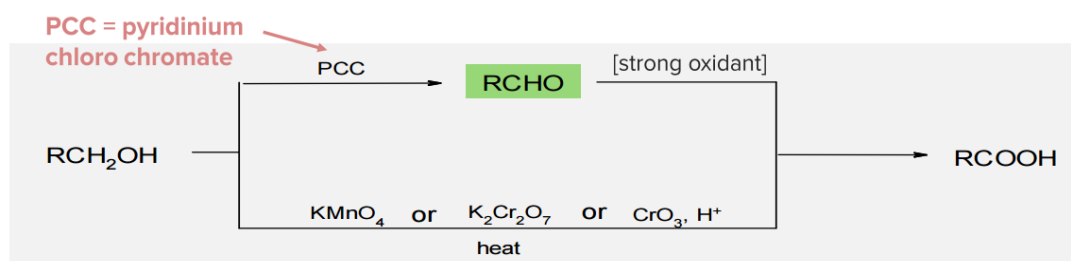
into acetaldehyde in the presence of the enzyme alcohol dehydrogenase.

Most of the time, biological oxidation of alcohol, and the reverse process, also require the presence of a coenzyme. Coenzymes are organic compounds that work with the enzyme to bring about the chemical change in the substrate. Coenzymes have functional groups complementary to that of the substrate, and the enzyme catalyzes the redox reaction in the substrate-coenzyme complex. In the process, ethanol is oxidized, and the original coenzyme is reduced. The coenzyme used for the biological oxidation of ethanol is an **oxidized form of nicotinamide adenine dinucleotide (NAD⁺)**. When the ethanol is converted to **acetaldehyde, NAD⁺ is reduced to NADH**.

Oxidation

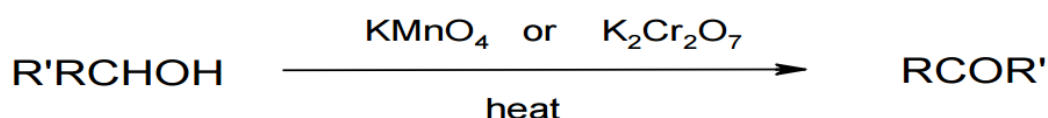
Note: Alcohol oxidation is very important in organic synthesis. There are different possible products, depending on whether the alcohol is 1, 2, 3.

- **1 alcohols** — the product depends on reaction conditions

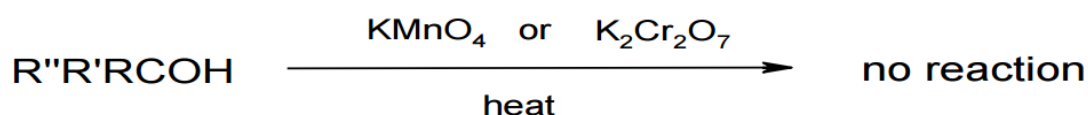


Note: In acidic conditions, dehydration might happen instead.

- **2 alcohols**



- **3 alcohols**

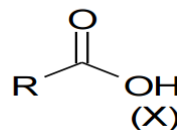
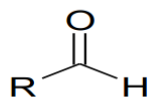
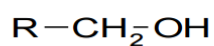
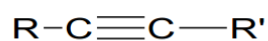
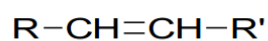
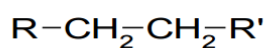


Oxidation and Reduction

Sometimes we also have H ions along, so reduction also becomes the gain of H and oxidation the loss of H.

(loss electrons)

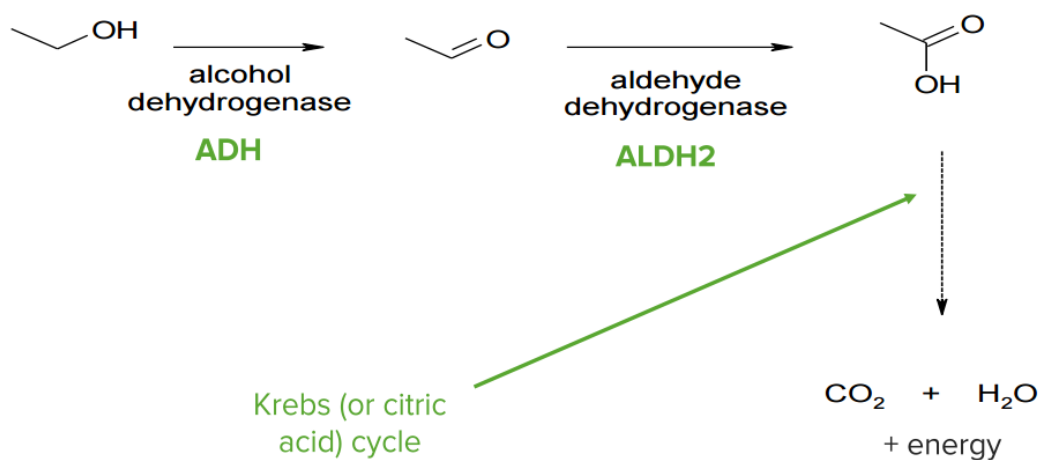
Oxidation



Reduction

(gain of electrons)

Alcohol Metabolism



References

McMurry, J. (2012). *Organic chemistry* (8th ed.). Belmont, CA: Cengage Learning Brooks/Cole.

Carey, F. A., & Giuliano, R. M. (2010). *Organic chemistry* (4th ed.). New York, NY: McGraw-Hill.

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