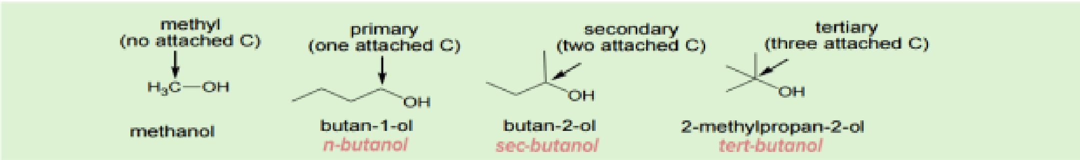
# Chemical Compound: Alcohols – General Formula and Functional Group

See online here

**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.


Alcohols are **any 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 wherein the C where the –OH group is attached to only one other carbon. Secondary alcohols, if the hydroxyl carbon is attached to two other carbon atoms and tertiary if attached to three other carbon atoms. **Below are the general structures of these three types of alcohol:**

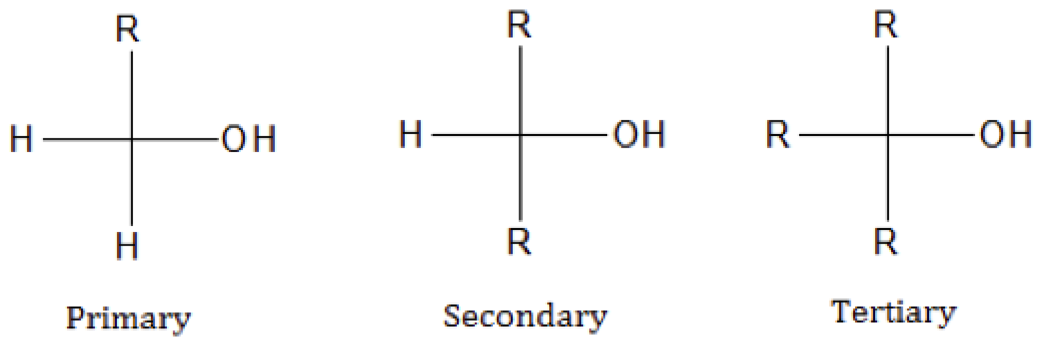
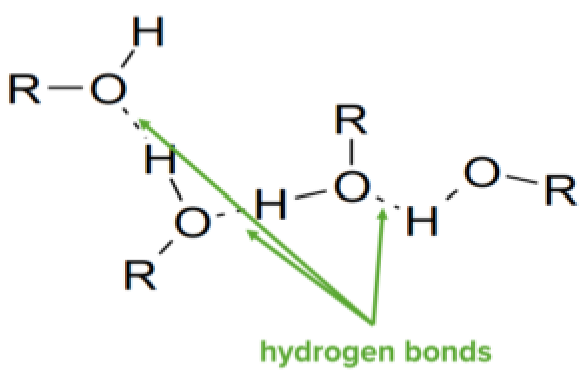



Figure: "Classes of Alcohols." by Mark Xavier Bailon.

Compared to the alkane, they have much **higher boiling points than the alkane of similar molecular weights**. This is because of their differences in the governing intermolecular forces of attraction (IMF) present for the two compounds. For alkane, the major IMF present is only the London Dispersion Forces.

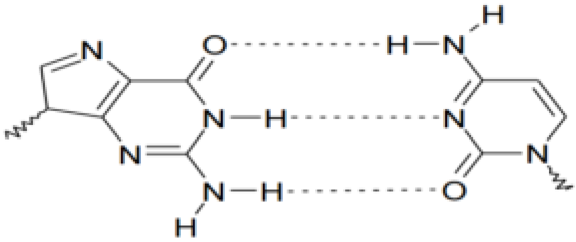
This is because of the non-polar nature of the compound. However, for alcohols, the presence of the -OH group enabled the compound to exhibit much stronger IMF in the form of hydrogen bonding.

**Hydrogen Bonds (H-bonds)** are formed when a Hydrogen atom bound to the small, highly electronegative atoms such as nitrogen, oxygen, and fluorine, forms an electrostatic attraction with another nearby highly electronegative atom (F, O, N). Because of the strong interaction between the H atom and the electronegative atom, molecules of alcohol are more attracted to each other and cause it to have a higher boiling point, compared to 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 % strength of a covalent bond, 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 a molecule. 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 their structure and properties. The double heliac structure of DNA, for example, is due largely to hydrogen bonding between the base pairs. Two strands of complementary bases are bonded together through the hydrogen bond. This 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 a-helix or the b-sheet secondary structure of proteins.

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

| nr C | Alkane | b.p. (°C) | Alcohol | b.p. (°C) |
|---|---|---|---|---|
| 1 | $CH_4$ | – 161 | $CH_3OH$ | 64.7 |
| 2 | $CH_3CH_3$ | – 88 | $CH_3CH_2OH$ | 78 |
| 3 | $CH_3CH_2CH_3$ | – 42 | $CH_3(CH_2)_2OH$ | 97 |
| 4 | $CH_3(CH_2)_2CH_3$ | – 0.5 | $CH_3(CH_2)_3OH$ | ≈ 116 |
| 5 | $CH_3(CH_2)_3CH_3$ | ≈ 35 | $CH_3(CH_2)_4OH$ | ≈ 136 |

**Note:** solubility: relatively high solubility 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 family of an organic compound is considered more reactive compared to the hydrocarbon counterpart. One of the important reactions of alcohol is its chemical transformation to produce an alkyl halide. For this reaction, alcohol reacts with a hydrogen halide and, in the process, the alkyl halide and water is produced.

**R-OH + H-X → R-X + H-OH**

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 kinetics of the reaction is also dependent 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.

**Reactivity to hydrogen halide:**

**Methyl ($CH_3OH$) < Primary ($RCH_3OH$) < Secondary ($R_2CHOH$) < Tertiary ($R_2COH$)**

Tertiary alcohols produce high yields with less amount of time compared to the 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 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. Because of the high instability of this intermediate, step 2 involves 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 elevated temperature.

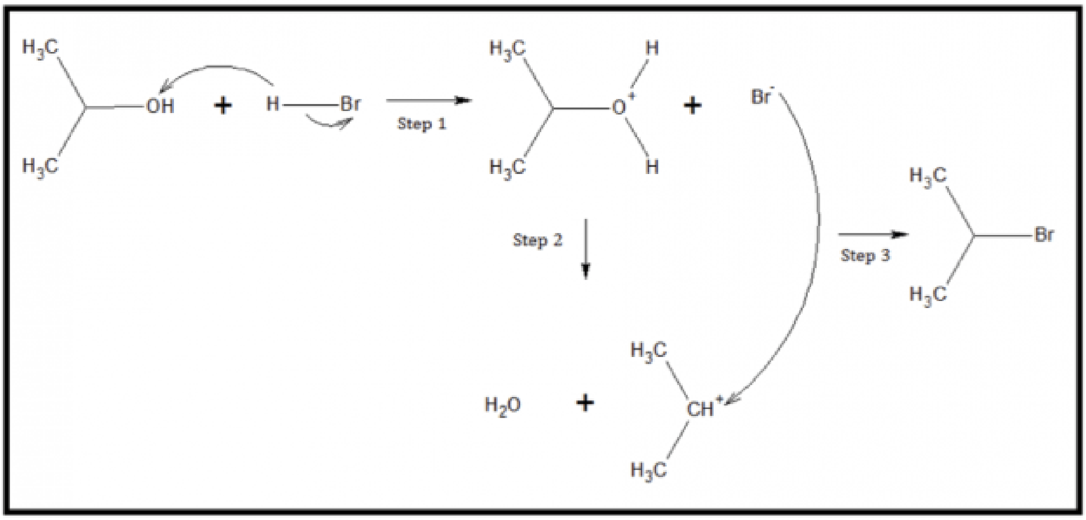



Figure: “Reaction of 2-propanol and HBr to produce 2-bromopropane.” by Mark Xavier Bailon.

# Elimination of Water

Another important reaction of alcohol is in the production of alkenes. The reaction proceeds with the elimination of water. Except for primary alcohols, reactions, just like in the other alkene preparation method, are said to be regioselective. That is a mixture of products that may form. Even though a mixture of products will be formed, the dehydration reaction of alcohol is stereoselective; that is it favors the production of the most stable stereoisomer.

Dehydration of alcohols is catalyzed by acid. This reaction requires the use of strong acids, like $H_2SO_4$, together with heating. The reaction also requires three steps. **Step 1 involves the attachment of a proton from the acid to the O atom of the –OH group forming the alkoxonium 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, 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.

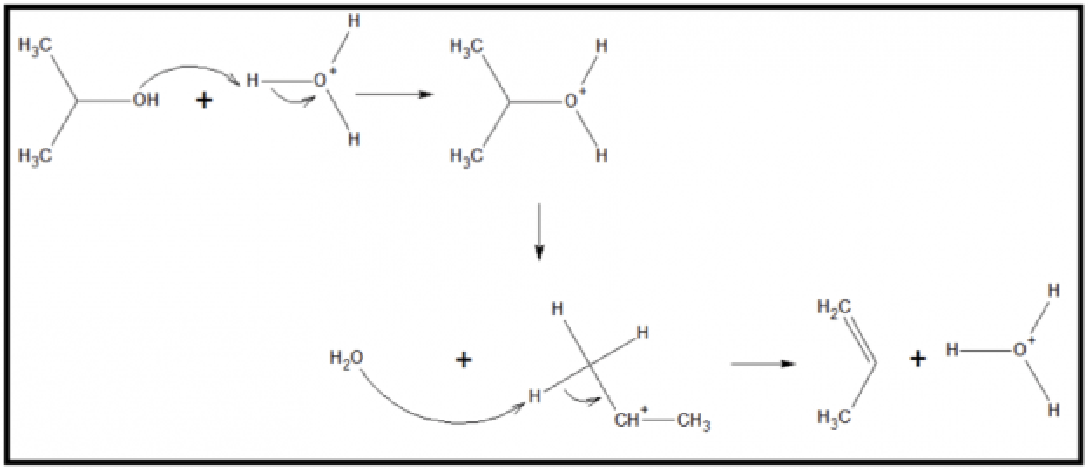
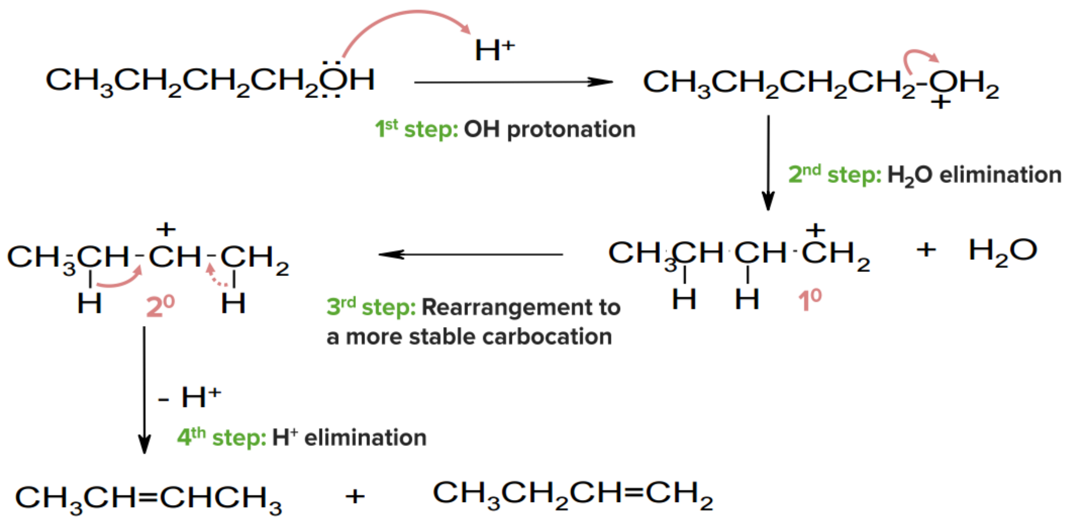


Figure: "Acid-catalyzed dehydration reaction of 2-propanol." by Mark Xavier Bailon.

## 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 because of steric reasons. Below is the trend for the reactivity of alcohol.

**Reactivity to Esterification:**

**Methyl ($CH_3OH$) > Primary ($RCH_2OH$) > Secondary ($R_2CHOH$) > Tertiary ($R_3COH$)**

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 the 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 from the structure. The last step involves the regeneration of the proton used up in the first step. The general mechanism for the reaction is described by the figure below.

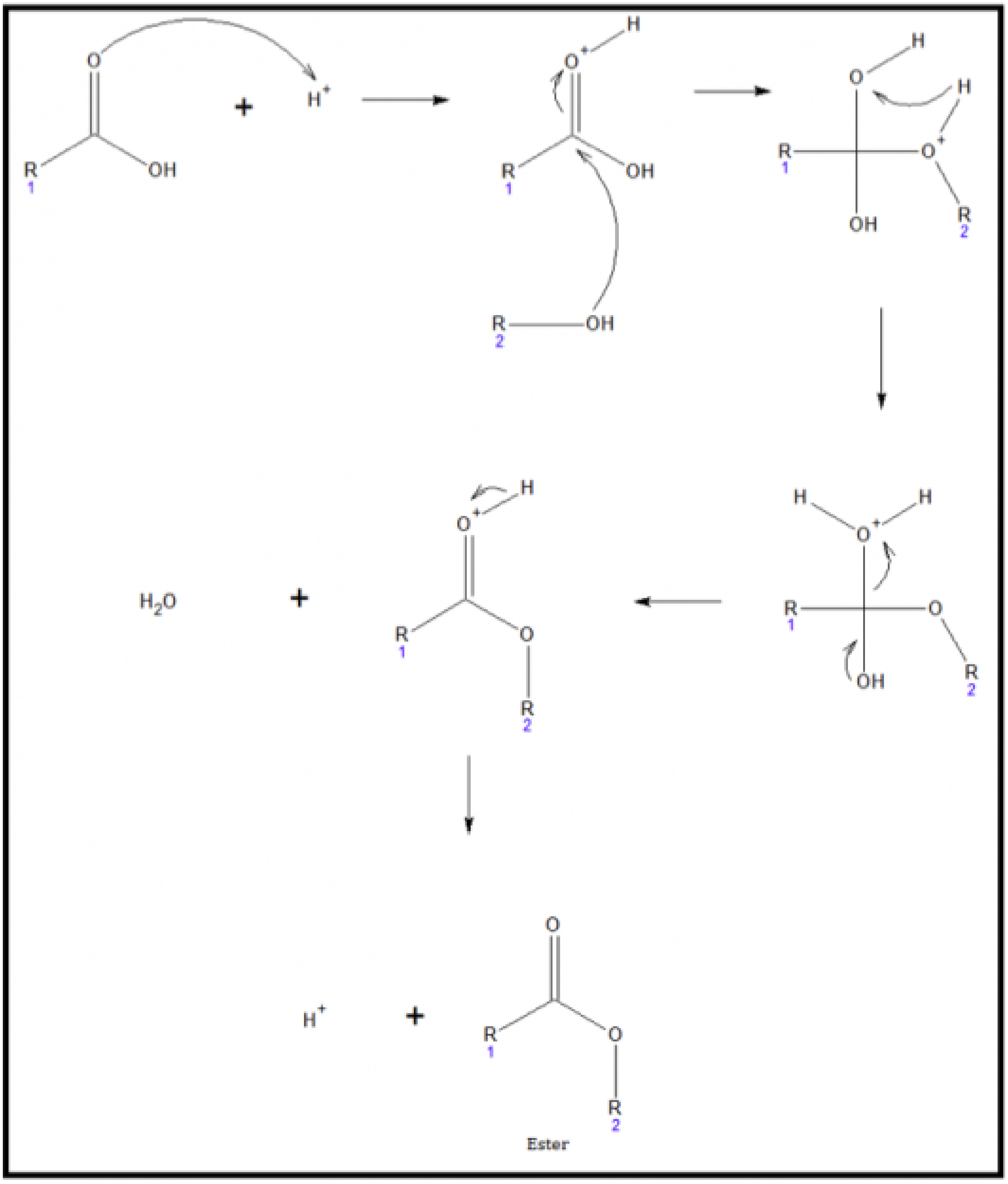



Figure: "Acid-catalyzed esterification." by Mark Xavier Bailon.

## 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 ($Cr_2O_7^{2-}$), pyridinium chlorochromate (PCC – $C_5H_5NH^+$ $ClCrO_3^-$ ), $C_5H_5NH^+$, and pyridinium dichromate (PDC – $(C_5H_5NH)_2^{2+}$ $Cr_2O_7^{2-}$).** Secondary alcohols are oxidized to ketones using the same set of reagents. Tertiary carbons cannot undergo oxidation as it doesn't have any hydrogen on their hydroxylbearing carbon.

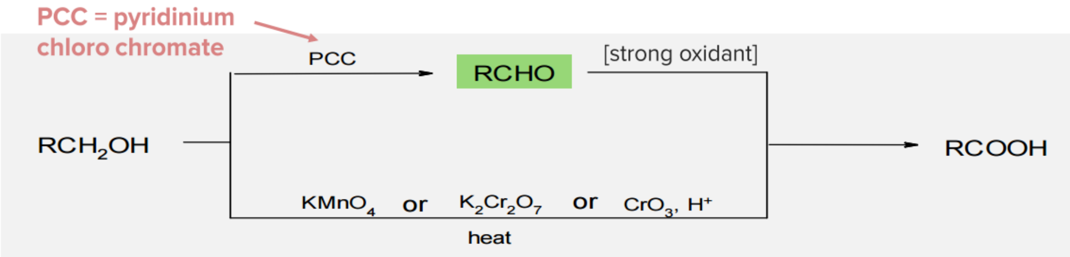
In biological systems, there are enzymes capable of inducing oxidation of alcohols and/or the reduction of carbonyl compounds to alcohols. For example, in the liver, ethanol may be metabolized into acetaldehyde in the presence of the enzyme alcohol dehydrogenase.

**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 with 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 ($NAD^+$)**. As 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 if the alcohol is 1, 2, 3.

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




**Note:** In acidic conditions dehydration might happen instead.

- **2 alcohols**

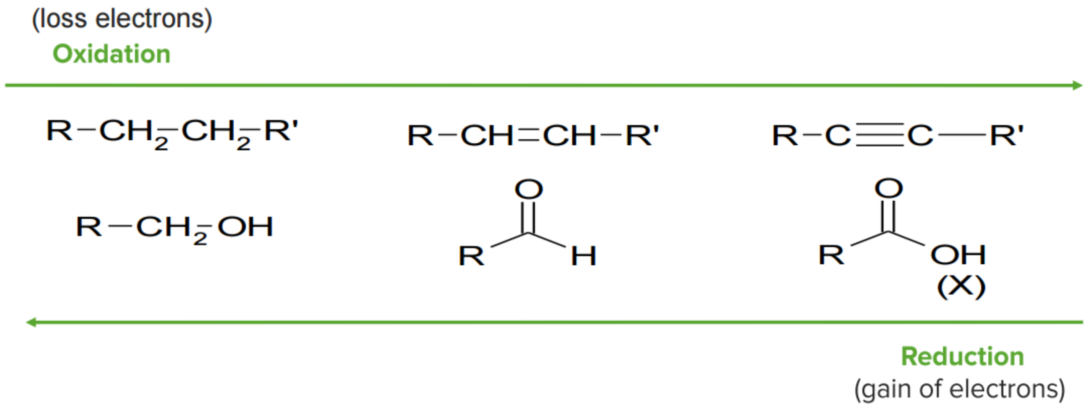
$$R'RCHOH \xrightarrow[\text{heat}]{KMnO_4 \quad \text{or} \quad K_2Cr_2O_7} RCOR'$$

- **3 alcohols**

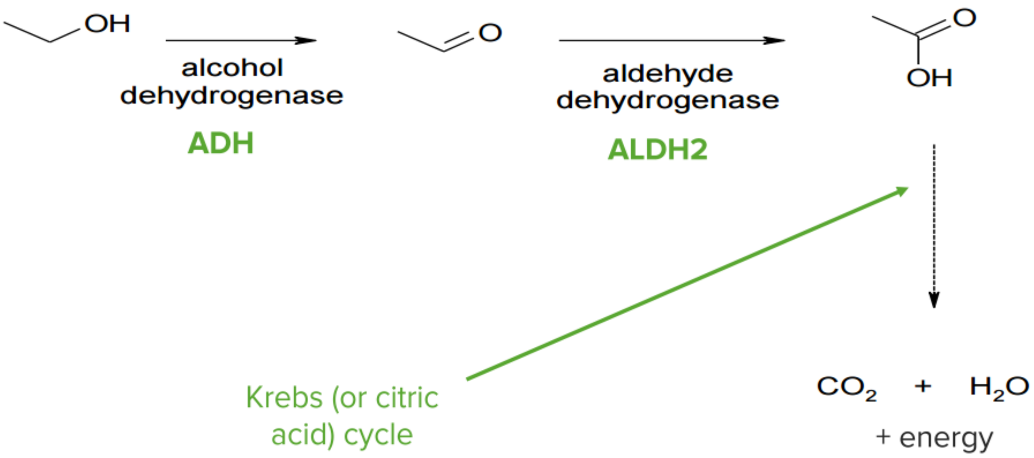
$$R''R'RCOH \xrightarrow[\text{heat}]{KMnO_4 \quad \text{or} \quad K_2Cr_2O_7} \text{no reaction}$$

## Oxidation and Reduction

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



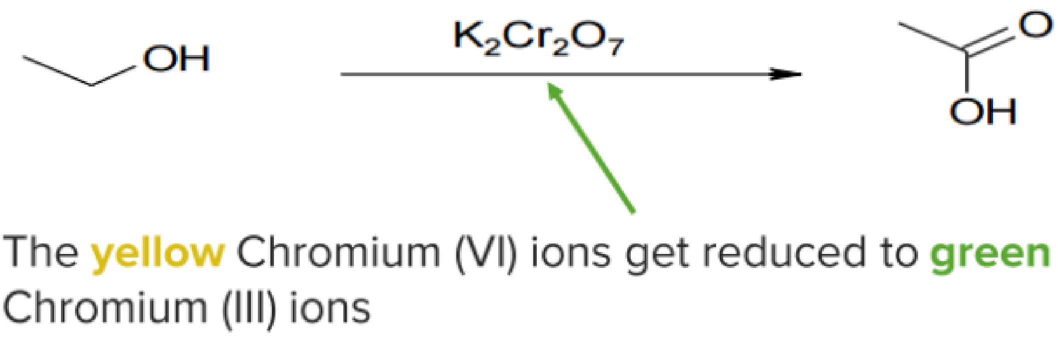

## Alcohol Metabolism




## Breathalyzer

The breathalyzer is a device for estimating blood alcohol content (BAC) from a breath sample.

**Note:** The BAC is measured through chemical oxidation and a light beam record the change of color.




**Uk Legal BAC:** 80 mg/100 ml

**Risk of coma:** BAC ≥ 500 mg/100 ml

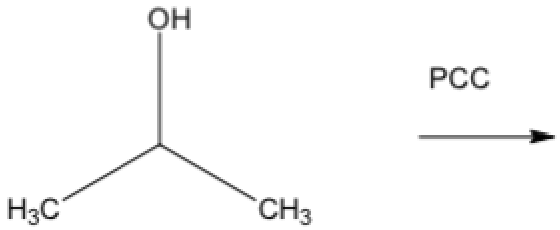
Newer breathalyzers use spectroscopic analysis (IR) of the breath trapped in the sample cell and measure and analyze the alcohol contained in it.

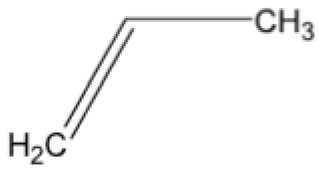
**Calculations:** About 2000 ml of breath contains the same amount of alcohol as 1 ml of blood.

## Review Questions

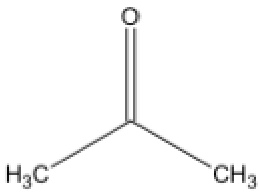
The answers are below the references.

**1. Which of the following will be produced when 2-propanol is oxidized by pyridinium chlorochromate (PCC)?**

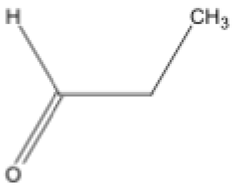




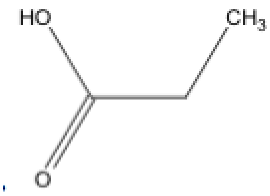
A.



B.



C.



D.

**2. What is the major intermolecular force of attraction present in alcohols?**

A. Dipole-Dipole
B. Ion-Dipole

C. Hydrogen Bonding
D. London Dispersion Forces

# 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.

**Correct answers:** 1B, 2C



Notes