# **Organic Chemistry I**

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## 8. Hydroxy Functional Group: Alcohols

Ethanol is a member of a large family of compounds called **alcohols**. The alcohols have carbon backbones bearing the substituent OH, the **hydroxy** functional group.

Alcohols may be viewed as derivatives of water in which one hydrogen has been replaced by an alkyl group. Replacement of the second hydrogen gives an **ether**.

The hydroxy function is readily converted to other functional groups, such as the C=C double bond in alkenes or the C=O bond in aldehydes and ketones.

Alcohols are abundant in nature and varied in structure. Simple alcohols are used as solvents; others aid in the synthesis of more complex molecules.



Water



Methanol (An alcohol)



Methoxymethane (Dimethyl ether) (An ether)

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#### **1 NAMING THE ALCOHOLS**

cohols may have both systematic and common names. Systematic nomenclature treats cohols as derivatives of alkanes. The ending *-e* of the alkane is replaced by **-ol.** Thus, an kane is converted into an **alkanol.** 

For example, the simplest alcohol is derived from methane: methanol. Ethanol stems from ethane, propanol from propane, and so on.

In more complicated, branched systems, the name of the alcohol is based on the longest chain *containing the OH substituent*—not necessarily the longest chain in the molecule.



To locate positions along the chain, number each carbon atom beginning from the end closest to the OH group. The names of other substituents along the chain can then be added to the alkanol stem as prefixes.

When there is more than one hydroxy substituent along the alkane stem, the molecule is called a diol, triol, and so on.



Cyclic alcohols are called **cycloalkanols.** Here the carbon carrying the functional group automatically receives the number 1.



When named as a substituent, the OH group is called *hydroxy*. This occurs when a functional group taking higher precedence, such as in hydroxycarboxylic acids, is present.

Like haloalkanes, alcohols can be classified as primary, secondary, or tertiary.



In common nomenclature, the name of the alkyl group is followed by the word *alcohol,* written separately. Common names are found in the older literature; although it is best not to use them, we should be able to recognize them.



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#### **8.2 STRUCTURAL AND PHYSICAL PROPERTIES OF ALCOHOLS**

The hydroxy functional group affects their molecular structure and allows them to enter into hydrogen bonding. It raises their boiling points and increases their solubilities in water.

#### The structure of alcohols resembles that of water

The structure of methanol resembles those of water and of methoxymethane (dimethyl ether). In all three, the bond angles reflect the effect of electron repulsion and increasing steric bulk of the substituents on the central oxygen. The two lone electron pairs are then placed into two nonbonding  $sp^3$  hybrid orbitals.

The O–H bond is considerably shorter than the C–H bond, because of the high electronegativity of oxygen relative to that of carbon. The electronegativity determines how tightly nuclei hold all their surrounding electrons, including the bonding electrons.

Consistent with this bond shortening is the order of bond strengths:  $DH_{O-H}^{\circ} = 104$  kcal mol<sup>-1</sup> (435 kJ mol<sup>-1</sup>);  $DH_{C-H}^{\circ} = 98$  kcal mol<sup>-1</sup> (410 kJ mol<sup>-1</sup>).



The electronegativity of oxygen causes an unsymmetrical distribution of charge in alcohols. This effect polarizes the O–H bond so that the hydrogen has a partial positive charge and gives rise to a molecular dipole, similar to that observed for water.

**Bond and Molecular Dipoles of Water and Methanol** 





Molecular dipole

Molecular dipole



#### Hydrogen bonding raises the boiling points and water solubilities of alcohols

Alcohols have unusually high boiling points, much higher than those of comparable alkanes and haloalkanes. The explanation lies in hydrogen bonding.

Hydrogen bonds may form between the oxygen atoms of one alcohol molecule and the hydroxy hydrogen atoms of another. Alcohols build up an extensive network of these interactions.

Although hydrogen bonds are longer and much weaker  $DH^8 = 5-6$  kcal mol<sup>-1</sup> (21-25 kJ mol<sup>-1</sup>) than the covalent O–H linkage ( $DH^\circ = 104$  kcal mol<sup>-1</sup>), so many of them form that their combined strength makes it difficult for molecules to escape the liquid. The result is a higher boiling point.

The effect is even more pronounced in water, which has two hydrogens available for hydrogen bonding.



Hydrogen bonding in water and alcohols is responsible for another property: Many alcohols are appreciably water soluble.

This behavior contrasts with that of the nonpolar alkanes, which are poorly solvated by this medium. Because of their characteristic insolubility in water, alkanes are said to be **hydrophobic** (*hydro*, Greek, water; *phobos*, Greek, fear).

The hydrophobic effect has its origin in two phenomena: (1) dissolution of alkyl chains in water requires breaking up the hydrogen-bonded network of the solvent, (2) the alkyl moieties can self-aggregate by London forces.

In contrast to the hydrophobic behavior of alkyl groups, the OH group and other polar substituents, such as COOH and NH<sub>2</sub>, are **hydrophilic**: They enhance water solubility.

As the values in Table 8-1 show, the larger the alkyl (hydrophobic) part of an alcohol, the lower its solubility in water. At the same time, the alkyl group increases the solubility of the alcohol in nonpolar solvents.

The "water-like" structure of the lower alcohols, particularly methanol and ethanol, makes them excellent solvents for polar compounds and even salts. It is not surprising that alcohols are popular *protic solvents* in the  $S_N2$  reaction.

#### Table 8-1 Physical Properties of Alcohols and Selected Analogous Haloalkanes and Alkanes

Compound	IUPAC name	Common name	Melting point (°C)	Boiling point (°C)	Solubility in H <sub>2</sub> O at 23°C
CH <sub>3</sub> OH	Methanol	Methyl alcohol	-97.8	65.0	Infinite
CH <sub>3</sub> Cl	Chloromethane	Methyl chloride	-97.7	-24.2	0.74 g/100 mL
CH <sub>4</sub>	Methane	•	-182.5	-161.7	3.5 mL (gas)/100 mL
CH <sub>3</sub> CH <sub>2</sub> OH	Ethanol	Ethyl alcohol	-114.7	78.5	Infinite
CH <sub>3</sub> CH <sub>2</sub> Cl	Chloroethane	Ethyl chloride	-136.4	12.3	0.447 g/100 mL
CH <sub>3</sub> CH <sub>3</sub>	Ethane	·	-183.3	-88.6	4.7 mL (gas)/100 mL
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	1-Propanol	Propyl alcohol	-126.5	97.4	Infinite
CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	Propane		-187.7	-42.1	6.5 mL (gas)/100 mL
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	1-Butanol	Butyl alcohol	-89.5	117.3	8.0 g/100 mL
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> OH	1-Pentanol	Pentyl alcohol	-79	138	2.2 g/100 mL

### 8.3 ALCOHOLS AS ACIDS AND BASES

Many applications of the alcohols depend on their ability to act both as acids and as bases. Thus, deprotonation gives alkoxide ions. Its structure affects  $pK_a$  values.

The lone electron pairs on oxygen render alcohols basic as well, and protonation results in alkyloxonium ions.

#### The acidity of alcohols resembles that of water

The acidity of alcohols in water is expressed by the equilibrium constant *K*.



Making use of the constant concentration of water (55 mol L<sup>-1</sup>), we derive a new equilibrium constant  $K_a$ .

$$K_{\rm a} = K[{\rm H}_2{\rm O}] = \frac{[{\rm H}_3{\rm O}^+][{\rm RO}^-]}{[{\rm ROH}]} \text{ mol } {\rm L}^{-1}, \text{ and } {\rm p}K_{\rm a} = -\log K_{\rm a}$$

Table 8-2 lists the  $pK_a$  values of several alcohols. A comparison of these values with those for mineral and other strong acids shows that alcohols, like water, are fairly weak acids. Their acidity is far greater than that of alkanes and haloalkanes.

The relatively strong electronegativity of the oxygen to the proton stabilizes the negative charge of the alkoxide ion.

Table 8-2	pK <sub>a</sub> Values of Alc	cohols in Water		
Compound	l p	pK <sub>a</sub>	Compound	p <i>K</i> <sub>a</sub>
НОН	1	5.7	ClCH <sub>2</sub> CH <sub>2</sub> OH	14.3
CH <sub>3</sub> OH	1	5.5	CF <sub>3</sub> CH <sub>2</sub> OH	12.4
CH <sub>3</sub> CH <sub>2</sub> OH	I 1	5.9	CF <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	14.6
$(CH_3)_2CHC$	<b>)</b> H 1	7.1	CF <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	15.4
$(CH_3)_3COH$	[ 1	.8		

To drive the equilibrium between alcohol and alkoxide to the side of the conjugate base, it is necessary to use a base *stronger* than the alkoxide formed (i.e., a base derived from a conjugate acid *weaker* than the alcohol):



This equilibrium lies well to the right ( $K < 10^{35-15.5} = 10^{19.5}$ ), because methanol is a much stronger acid than is ammonia, or, conversely, because amide is a much stronger base than is methoxide.

It is sometimes sufficient to generate alkoxides in less than stoichiometric equilibrium concentrations:

$$CH_{3}CH_{2}\overset{\bullet}{O} \stackrel{\bullet}{\longrightarrow} H + Na^{+-} \overset{\bullet}{:} \overset{\bullet}{O}H \stackrel{K}{\Longrightarrow} CH_{3}CH_{2}\overset{\bullet}{O} \overset{\bullet}{:} Na^{+} + H_{2}\overset{\bullet}{O}$$

$$pK_{a} = 15.9$$

$$pK_{a} = 15.7$$

#### Steric disruption and inductive effects control the acidity of alcohols

The acidity decreases ( $pK_a$  increases) from methanol to primary, secondary, and finally tertiary systems.

This ordering has been ascribed to steric disruption of **solvation** and to **hydrogen bonding** in the alkoxide, which are stabilized the negative charge on oxygen, interference with these processes leads to an increase in  $pK_a$ .

