1.5 Aldehydes and Ketones

Saffron, produced from the stamens of the crocus flower, is the most expensive spice on Earth (**Figure 1**). The cost per gram of saffron is approximately equal to that of silver. An organic compound, safranal, is responsible for its characteristic aroma. The compounds responsible for the scents of saffron and many other spices, including cumin, vanilla, cinnamon, and ginger, all have a similar functional group: carbonyl. Not surprisingly, scents and perfumes contain many compounds with carbonyl groups. The solvents in some paint and fingernail polish removers, lacquers, and glues also have carbonyl groups. WEB LINK

Figure 1 The stamens of crocus flowers are removed and dried for use as the spice saffron.

carbonyl group a carbon atom double-bonded to an oxygen atom, found in organic compounds such as aldehydes and ketones

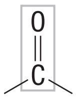


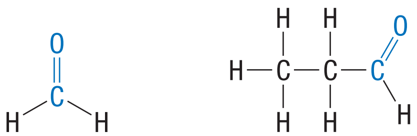
Figure 2 A carbonyl group

aldehyde an organic molecule containing a carbonyl group that is bonded to at least 1 hydrogen atom

The Carbonyl Group

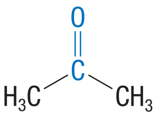
Aldehydes and ketones both contain the carbonyl group. A **carbonyl group** is an atom of carbon double-bonded to an atom of oxygen (**Figure 2**). The carbonyl group is the functional group responsible for the properties of ketones and aldehydes. The difference between the two classes of compound is the location of the carbonyl group within the molecule.

In an **aldehyde**, the carbonyl group is bonded to at least 1 hydrogen atom, which means that it is located at the end of the parent chain of the molecule. In the simplest aldehyde, methanal (also called formaldehyde), the carbon of the carbonyl group is the only carbon atom in the molecule (**Figure 3**). In longer molecules, such as butanal, the carbonyl group is at the end.



(a) methanal (b) propanal

Figure 3 The carbonyl group is always at the end of the carbon chain in an aldehyde molecule.



propanone; a ketone

Figure 4 The carbonyl group is always attached to 2 other carbon atoms in the carbon chain in a ketone molecule.

ketone an organic compound that contains a carbonyl group bonded to 2 carbon atoms

A **ketone** is an organic compound whose molecules have a carbonyl group bonded to 2 carbon atoms in the carbon chain. The simplest ketone is propanone (also known as acetone), which has 3 carbon atoms including the one in the carbonyl group. Compare the structure of propanone (**Figure 4**) with the structure of propanal (Figure 3(b)).

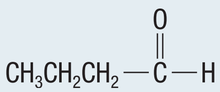
Naming Aldehydes and Ketones

The naming of aldehydes and ketones follows conventions similar to those of the compounds discussed in earlier sections. For an aldehyde, replace the final *-e* from the name of the parent alkane with the suffix *-al*. As Figure 3(a) shows, the simplest aldehyde contains only the carbonyl group bonded to 2 hydrogen atoms. Its parent alkane is methane, so the aldehyde is called methanal. Position numbers are not used in naming aldehydes because the carbonyl group is always designated as carbon number 1 in the chain.

Tutorial 1 Naming and Drawing Aldehydes

Sample Problem 1: Naming Aldehydes from Structural Formulas

Name the following compound:



Solution

First, determine the name of the base alkane. This compound has a 4-carbon parent chain, so it is based on the alkane butane. The name of the corresponding aldehyde is butanal.

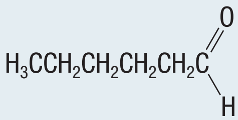
Sample Problem 2: Drawing Aldehydes

Draw the structure of each of the following molecules:

(a) hexanal (b) 7-hydroxyoctanal

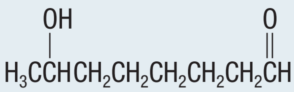
Solution (a)

Hexanal is based on hexane. The suffix *-al* tells us that the compound is an aldehyde, so it has a carbonyl group at one end (carbon atom number 1) of the carbon chain.



Solution (b)

7-hydroxyoctanal is based on octane. The carbonyl group is located on carbon atom number 1 and a hydroxyl group is located on carbon atom number 7.

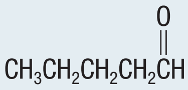


When representing molecules that have several carbon atoms, chemists sometimes use a convention called line diagrams. These are a "shorthand" form of structural diagrams in which the carbon atoms and their attached hydrogen atoms are not shown. Instead, you assume that there is a carbon atom at the end of each line and at every bend in the line, and that each carbon atom is surrounded by the maximum possible number of hydrogen atoms. The following Practice questions include an example of a line diagram.

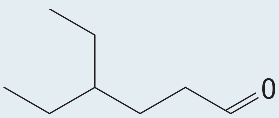
Practice

1. Name each of the following aldehydes: K/U

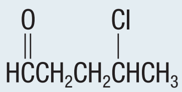
(a)



(b)



(c)



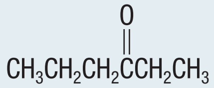
2. Draw the structure of each of the following aldehydes: K/U C
   (a) butanal
   (b) 4-methylpentanal
   (c) 2-hydroxybutanal

To name a ketone, the *-e* of the parent alkane is replaced with the suffix *-one*. The simplest ketone, shown in Figure 4, has 3 carbon atoms. Its name, derived from propane, is propanone. For ketones with 5 or more carbon atoms, the position of the carbonyl is designated by the number of the carbon atom of the carbonyl group. As usual, we assign the lowest possible number.

Tutorial 2 Naming and Drawing Ketones

Sample Problem 1: Naming Ketones from Structural Formulas

Name the ketone shown below.



Solution

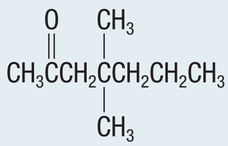
First, identify the parent alkane: hexane. Then, number the carbon atoms to give the carbonyl group the lowest possible number. This compound is hexan-3-one.

Sample Problem 2: Drawing Ketones

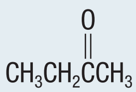
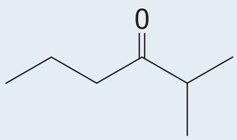
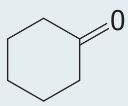
Draw the structural formula for 4,4-dimethyl-heptan-2-one.

Solution

First, draw the carbon chain for the parent alkane: heptane. Then, draw the carbonyl group attached to the appropriate carbon atom. Next, add the other substituent groups—two methyl groups—to their carbon atoms. Finally, add hydrogen atoms to the remaining carbon atoms so that each carbon has four bonds.



Practice

1. Name the following ketones: K/U
   (a)
   
   (b)
   
   (c)
   

2. Draw the structures for the following ketones: K/U C
   (a) 4-methylheptan-3-one
   (b) 1,3-dichlorobutan-2-one
   (c) heptane-3,5-dione
   (d) cyclobutanone
   (e) 4-hydroxypentan-2-one

Properties of Aldehydes and Ketones

The chemical and physical properties of aldehydes and ketones are affected by the carbonyl group. Because oxygen has a much higher electronegativity than carbon, electrons from the double bond are attracted to the oxygen atom. As a result, the molecules are polar. They have dipole–dipole attractions but, since the molecules do not contain a hydroxyl group, they do not form hydrogen bonds with one another. Therefore, their boiling points are lower than similar alcohols. The presence of the carbonyl oxygen does allow aldehydes and ketones to form attractions with water molecules, so these molecules are more soluble in water than are alkanes, but less soluble than are similarly sized alcohol molecules. Small aldehydes and ketones are completely soluble in water, but the solubility decreases as additional carbons are added to the chain. Aldehydes and ketones are often used as solvents in industrial processes.

UNIT TASK BOOKMARK

Propanone (acetone) is a VOC that is widely used as a solvent. Consider its pros and cons as you work on the Unit Task, described on page 116.

Reactions Involving Aldehydes and Ketones

Historically, reactions in which oxygen is a reactant were referred to as oxidation reactions. The term has since come to have a broader meaning, including those reactions in which a substance loses electrons. The chemistry of these reactions will be discussed in Unit 5.

Formation of Aldehydes and Ketones: Controlled Oxidation

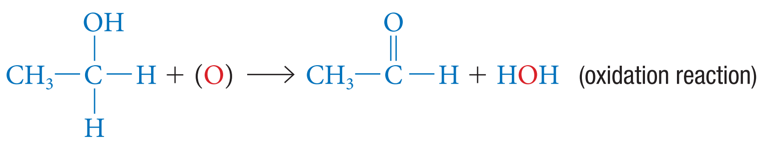
Aldehydes and ketones are synthesized by the controlled oxidation of alcohol. In a complete oxidation reaction (combustion reaction) of alcohol, the products are carbon dioxide and water. Thermal energy is also released.

In the controlled oxidation of an alcohol, the reactant is not completely oxidized. If there is only a limited quantity of oxygen present, an aldehyde or ketone is produced. In these types of reactions, oxygen atoms can be supplied by air or by compounds known as oxidizing agents. The balanced chemical equation for the reaction of ethanol with oxygen from the air is

$$2\ C_2H_5OH(l) + O_2(g) \rightarrow 2\ C_2H_4O(l) + 2\ H_2O(l)$$

Oxidizing agents are oxygen-rich compounds such as potassium dichromate, K_2Cr_2O hydrogen peroxide, H_2O_2, and potassium permanganate, $KMnO_4$. To keep the equations simple, we often use (O) to represent the oxidizing agent in an oxidation reaction.

When a primary alcohol is oxidized, the oxygen atom and one of the hydrogen atoms remain on the carbon atom, resulting in a carbonyl group on the terminal carbon atom, an aldehyde. The 2 hydrogen atoms that were removed bond with oxygen from the oxidizing agent. For example, the controlled oxidation of ethanol (a primary alcohol) produces ethanal and water:

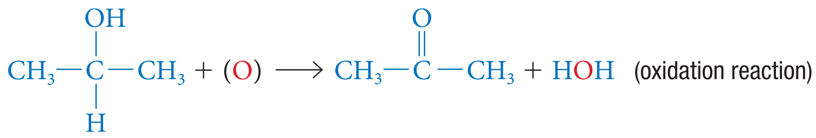


ethanol (1° alcohol) ethanal (aldehyde) water

Investigation 1.5.1

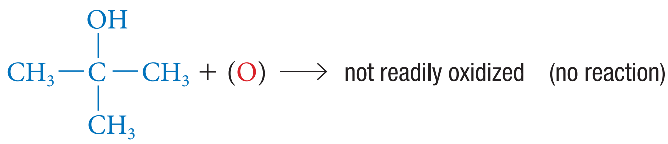
Reactions of Three Isomers of Butanol (page 64)
Now that you have studied the reactions of various alcohol isomers, you have an opportunity to investigate how the structures of alcohol molecules affect their chemical characteristics.

A secondary alcohol will also form a carbonyl group, producing a ketone rather than aldehyde. One hydrogen atom is removed from the hydroxyl group and the second comes from the carbon atom to which the hydroxyl group is bonded. The controlled oxidation of propan-2-ol produces propanone and water:



propan-2-ol (2° alcohol) | propanone (ketone) | water

Tertiary alcohols do not react in the same way because no hydrogen atom is available on an adjacent carbon atom. An example is the attempted oxidation of 2-methylpropan-2-ol:

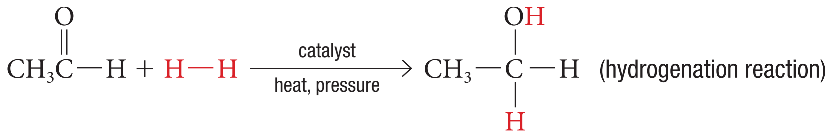


2-methylpropan-2-ol (3° alcohol)

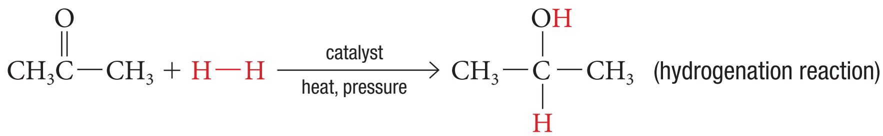
To summarize the controlled oxidation reactions of alcohols, a primary alcohol produces an aldehyde, a secondary alcohol produces a ketone, and a tertiary alcohol does not easily oxidize.

Hydrogenation of Aldehydes and Ketones

Recall from Section 1.2 that a hydrogenation reaction involves the addition of hydrogen to another molecule. In the hydrogenation reaction of an aldehyde or a ketone, the net result is that a double bond is broken. One hydrogen atom is added to the oxygen atom and another is added to the carbon atom to which the oxygen is bonded. Hydrogenation of aldehydes or ketones occurs only under conditions of high temperature and pressure, and the presence of a catalyst. The product of this reaction is an alcohol. For example, hydrogenation of ethanal forms ethanol, and hydrogenation of propanone forms propan-2-ol. These are the reverse of the oxidation of alcohols. The hydrogenation of the aldehyde produces a primary alcohol, and the hydrogenation of a ketone produces a secondary alcohol:



ethanal (aldehyde) | ethanol (primary alcohol)



propanone (ketone) | 2-propanol (secondary alcohol)

Tutorial 3 Reactions Involving Aldehydes and Ketones

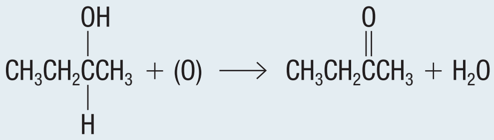
In this tutorial you will explore reactions involving aldehydes and ketones as both reactants and products.

Sample Problem 1: Preparing Aldehydes and Ketones from Alcohols

Draw the structural formula equations for the reactions that produce butanone and butanal.

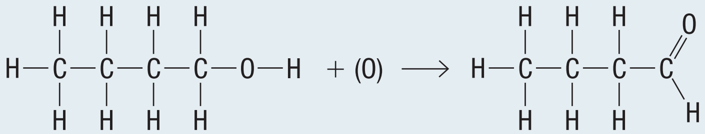
Solution

Butanone and butanal both have 4-carbon backbones. Both can be formed by the controlled oxidation of a 4-carbon alcohol. Ketones form from a secondary alcohol, so butanone will form during the controlled oxidation of butan-2-ol:



butan-2-ol butanone

Aldehydes form during the oxidation of primary alcohols, so to form butanal, butan-1-ol needs to react with oxygen:



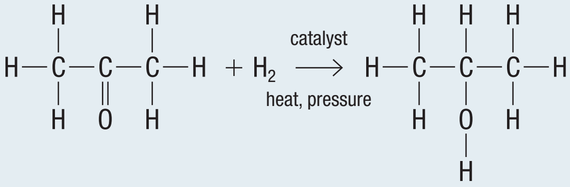
butan-1-ol butanal

Sample Problem 2: Producing an Alcohol from a Ketone

Draw the structural formula equation representing the hydrogenation of propanone.

Solution

The hydrogenation of a ketone produces a secondary alcohol. Therefore, the hydrogenation of propanone will form propan-2-ol:



propanone propan-2-ol

Practice

1. Name the reactants required to produce each of the following compounds, then illustrate the reactions using structural formulas. K/U C
   (a) pentanone
   (b) pentanal
2. Name the products resulting from the hydrogenation of each of the following compounds, then illustrate the reactions using structural formulas. K/U C
   (a) ethanal
   (b) butanone
3. Predict the products of the controlled oxidation of the following isomers: K/U
   (a) hexan-1-ol
   (b) hexan-2-ol
   (c) 2-methylpentan-2-ol

1.5 Review

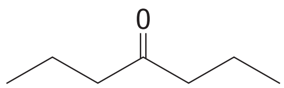
Summary

- If a carbonyl group is attached to at least 1 hydrogen atom, the molecule is an aldehyde. It is named using the suffix *-al*.
- If a carbonyl group is attached to 2 carbon atoms, the molecule is a ketone. It is named using the suffix *-one*.
- The carbonyl group (C=O) makes organic molecules polar, giving them higher boiling points and greater water solubility than the corresponding alkanes.
- The controlled oxidation of a primary alcohol produces an aldehyde. The controlled oxidation of a secondary alcohol produces a ketone. Tertiary alcohols do not readily undergo controlled oxidation.
- The hydrogenation of an aldehyde produces a primary alcohol. The hydrogenation of a ketone produces a secondary alcohol.

Questions

1. Copy and complete **Table 1** in your notebook. T/I C
2. Using the condensed structural formulas, write a chemical equation for the controlled oxidation of the following alcohols. Write the IUPAC name for each product. T/I
   (a) pentan-2-ol
   (b) hexan-1-ol
3. (a) Design a procedure to prepare an alcohol from propanone. Describe the main steps in the procedure and the conditions needed.
   (b) Write a chemical equation to represent the reaction. T/I C
4. You have been asked to prepare a sample of ethanal from an alcohol. K/U T/I
   (a) What alcohol will you use as your reactant? Explain.
   (b) Describe the main steps in the procedure and the conditions needed to prepare ethanal.
   (c) Draw or write a chemical equation to represent the reaction.
5. Design an experimental procedure that you could carry out to allow you to distinguish a tertiary alcohol from a primary or secondary alcohol. T/I A

Table 1

Name	Condensed structure	Line diagram or structural formula	Type of compound
	$CH_3CH_2CH_2CH_2CH_2CH_2CHO$		
			
	$CH_3CH_2COCH_2CH_3$		
1-chlorobutan-2-one			
3-methylpentanal