

15: ALDEHYDES AND KETONES



CHAPTER OVERVIEW

15: Aldehydes and Ketones

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15.5: Oxidation of Aldehydes

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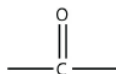
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15.1: The Carbonyl Group

Learning Objective

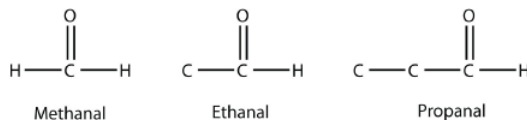
- Identify the aldehyde and ketone functional groups.

There are other functional groups that contain O atoms. Before we introduce them, we define the **carbonyl group**, which is formed when an O atom and a C atom are joined by a double bond:



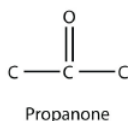
The other two bonds on the C atom are attached to other atoms. It is the identities of these other atoms that define what specific type of compound an organic molecule is.

If one bond of the carbonyl group is made to an H atom, then the molecule is classified as an **aldehyde** (If there are two H atoms, there is only 1 C atom). When naming aldehydes, the main chain of C atoms must include the carbon in the carbonyl group, which is numbered as position 1 in the carbon chain. The parent name of the hydrocarbon is used, but the suffix *-al* is appended. (Do not confuse *-al* with *-ol*, which is the suffix used for alcohols.) So we have

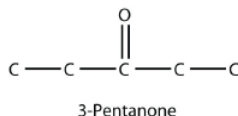


Methanal has a common name with which you may be familiar: formaldehyde. The main thing to note about aldehydes is that the carbonyl group is at the *end* of a carbon chain.

A carbonyl group in the middle of a carbon chain implies that both remaining bonds of the carbonyl group are made to C atoms. This type of molecule is called a **ketone**. Despite the fact that aldehydes and ketones have the same carbonyl group, they have different chemical and physical properties and are properly grouped as two different types of compounds. The smallest ketone has three C atoms in it. When naming a ketone, we take the name of the parent hydrocarbon and change the suffix to *-one*:



The common name for propanone is acetone. With larger ketones, we must use a number to indicate the position of the carbonyl group, much like a number is used with alkenes and alkynes:



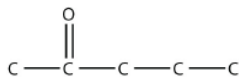
There is another way to name ketones: name the alkyl groups that are attached to the carbonyl group and add the word *ketone* to the name. So propanone can also be called dimethyl ketone, while 2-butanone is called methyl ethyl ketone.

✓ Example 15.1.1

Draw the structure of 2-pentanone.

Solution

This molecule has five C atoms in a chain, with the carbonyl group on the second C atom. Its structure is as follows:



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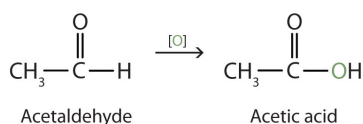
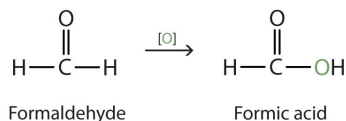
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15.2: Naming Aldehydes and Ketones

Learning Objectives

- Use the IUPAC system to name and draw aldehydes and ketones.

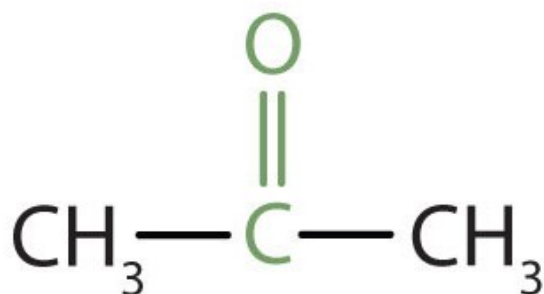
Both common and International Union of Pure and Applied Chemistry (IUPAC) names are frequently used for aldehydes and ketones, with common names predominating for the lower homologs. The common names of aldehydes are taken from the names of the acids into which the aldehydes can be converted by *oxidation*.



The stems for the common names of the first four aldehydes are as follows:

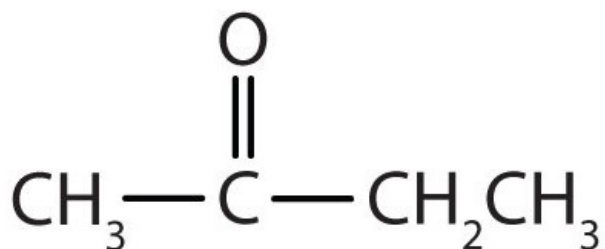
- 1 carbon atom: *form-*
- 2 carbon atoms: *acet-*
- 3 carbon atoms: *propion-*
- 4 carbon atoms: *butyr-*

Because the carbonyl group in a ketone must be attached to two carbon groups, the simplest ketone has three carbon atoms. It is widely known as *acetone*, a unique name unrelated to other common names for ketones.



Acetone

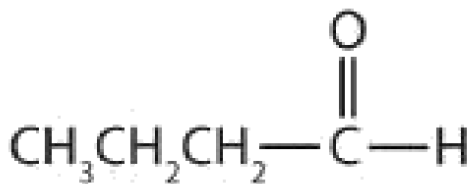
Generally, the common names of ketones consist of the names of the groups attached to the carbonyl group, followed by the word *ketone*. (Note the similarity to the naming of ethers.) Another name for acetone, then, is *dimethyl ketone*. The ketone with four carbon atoms is ethyl methyl ketone.



Ethyl methyl ketone

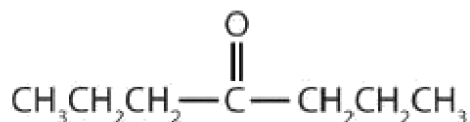
✓ Example 15.2.1

Classify each compound as an aldehyde or a ketone. Give the common name for each ketone.

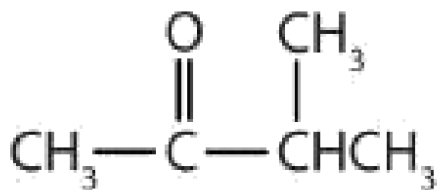


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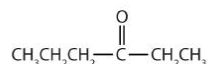
Solution

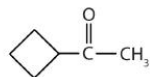
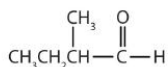
1. This compound has the carbonyl group on an end carbon atom, so it is an aldehyde.
2. This compound has the carbonyl group on an interior carbon atom, so it is a ketone. Both alkyl groups are propyl groups. The name is therefore dipropyl ketone.
3. This compound has the carbonyl group between two alkyl groups, so it is a ketone. One alkyl group has three carbon atoms and is attached by the middle carbon atom; it is an isopropyl group. A group with one carbon atom is a methyl group. The name is therefore isopropyl methyl ketone.

? Exercise 15.2.1

Classify each compound as an aldehyde or a ketone. Give the common name for each ketone.

1.

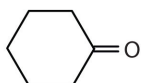
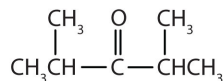




Here are some simple IUPAC rules for naming aldehydes and ketones:

✓ Example 15.2.2

Give the IUPAC name for each compound.

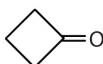
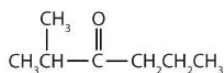


Solution

- There are five carbon atoms in the LCC. The methyl group (CH_3) is a substituent on the second carbon atom of the chain; the aldehyde carbon atom is always C1. The name is derived from pentane. Dropping the *-e* and adding the ending *-al* gives pentanal. The methyl group on the second carbon atom makes the name 2-methylpentanal.
- There are five carbon atoms in the LCC. The carbonyl carbon atom is C3, and there are methyl groups on C2 and C4. The IUPAC name is 2,4-dimethyl-3-pentanone.
- There are six carbon atoms in the ring. The compound is cyclohexanone. No number is needed to indicate the position of the carbonyl group because all six carbon atoms are equivalent.

? Exercise

Give the IUPAC name for each compound.



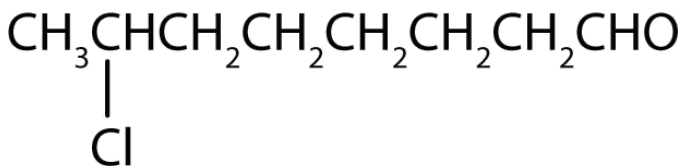
✓ Example 15.2.3

Draw the structure for each compound.

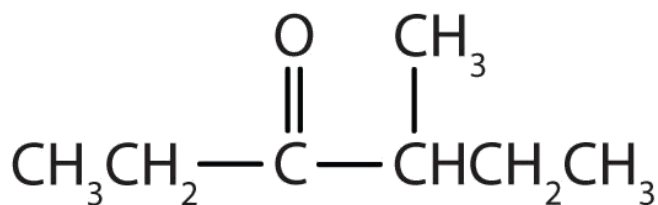
- 7-chlorooctanal
- 4-methyl-3-hexanone

Solution

- The *octan-* part of the name tells us that the LCC has eight carbon atoms. There is a chlorine (Cl) atom on the seventh carbon atom; numbering from the carbonyl group and counting the carbonyl carbon atom as C1, we place the Cl atom on the seventh carbon atom.



- The *hexan-* part of the name tells us that the LCC has six carbon atoms. The 3 means that the carbonyl carbon atom is C3 in this chain, and the 4 tells us that there is a methyl (CH₃) group at C4:



? Exercise

Draw the structure for each compound.

- 5-bromo-3-iodoheptanal
- 5-bromo-4-ethyl-2-heptanone

Concept Review Exercises

Summary

The common names of aldehydes are taken from the names of the corresponding carboxylic acids: formaldehyde, acetaldehyde, and so on. The common names of ketones, like those of ethers, consist of the names of the groups attached to the carbonyl group, followed by the word *ketone*. Stem names of aldehydes and ketones are derived from those of the parent alkanes, using an *-al* ending for an aldehydes and an *-one* ending for a ketone.

- The stem names of aldehydes and ketones are derived from those of the parent alkanes, defined by the longest continuous chain (LCC) of carbon atoms that contains the functional group.
- For an aldehyde, drop the *-e* from the alkane name and add the ending *-al*. Methanal is the IUPAC name for formaldehyde, and ethanal is the name for acetaldehyde.
- For a ketone, drop the *-e* from the alkane name and add the ending *-one*. Propanone is the IUPAC name for acetone, and butanone is the name for ethyl methyl ketone.
- To indicate the position of a substituent on an aldehyde, the carbonyl carbon atom is always considered to be C1; it is unnecessary to designate this group by number.

5. To indicate the position of a substituent on a ketone, number the chain in the manner that gives the carbonyl carbon atom the lowest possible number. In cyclic ketones, it is understood that the carbonyl carbon atom is C1.
6. Give the structure and IUPAC name for the compound that has the common name *m*-bromobenzaldehyde.
7. Give the IUPAC name for glyceraldehyde, (HOCH₂CHOHCHO). (Hint: as a substituent, the OH group is named *hydroxy*.)

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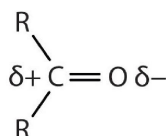
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15.3: Properties of Aldehydes and Ketones

Learning Objectives

- Explain why the boiling points of aldehydes and ketones are higher than those of ethers and alkanes of similar molar masses but lower than those of comparable alcohols.
- Compare the solubilities in water of aldehydes and ketones of four or fewer carbon atoms with the solubilities of comparable alkanes and alcohols.
- Name the typical reactions that take place with aldehydes and ketones.
- Describe some of the uses of common aldehydes and ketones.

The carbon-to-oxygen double bond is quite polar, more polar than a carbon-to-oxygen single bond. The electronegative oxygen atom has a much greater attraction for the bonding electron pairs than does the carbon atom. The carbon atom has a partial positive charge, and the oxygen atom has a partial negative charge:



In aldehydes and ketones, this charge separation leads to dipole-dipole interactions that are great enough to significantly affect the boiling points. Table 15.3.1 shows that the polar single bonds in ethers have little such effect, whereas hydrogen bonding between alcohol molecules is even stronger.

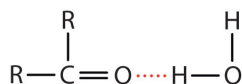
Table 15.3.1: Boiling Points of Compounds Having Similar Molar Masses but Different Types of Intermolecular Forces

Compound	Family	Molar Mass	Type of Intermolecular Forces	Boiling Point (°C)
CH ₃ CH ₂ CH ₂ CH ₃	alkane	58	dispersion only	-1
CH ₃ OCH ₂ CH ₃	ether	60	weak dipole	6
CH ₃ CH ₂ CHO	aldehyde	58	strong dipole	49
CH ₃ CH ₂ CH ₂ OH	alcohol	60	hydrogen bonding	97

Formaldehyde is a gas at room temperature. Acetaldehyde boils at 20°C; in an open vessel, it boils away in a warm room. Most other common aldehydes are liquids at room temperature.

Although the lower members of the homologous series have pungent odors, many higher aldehydes have pleasant odors and are used in perfumes and artificial flavorings. As for the ketones, acetone has a pleasant odor, but most of the higher homologs have rather bland odors.

The oxygen atom of the carbonyl group engages in hydrogen bonding with a water molecule.

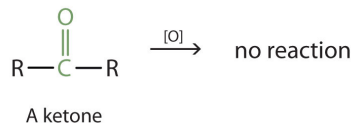
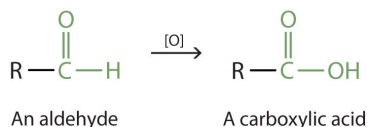


The solubility of aldehydes is therefore about the same as that of alcohols and ethers. Formaldehyde, acetaldehyde, and acetone are soluble in water. As the carbon chain increases in length, solubility in water decreases. The borderline of solubility occurs at about four carbon atoms per oxygen atom. All aldehydes and ketones are soluble in organic solvents and, in general, are less dense than water.

Oxidation of Aldehydes and Ketones

Aldehydes and ketones are much alike in many of their reactions, owing to the presence of the carbonyl functional group in both. They differ greatly, however, in one most important type of reaction: oxidation. Aldehydes are readily oxidized to carboxylic acids,

whereas ketones resist oxidation.



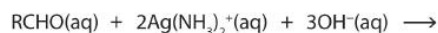
The aldehydes are, in fact, among the most easily oxidized of organic compounds. They are oxidized by oxygen (O₂) in air to carboxylic acids.



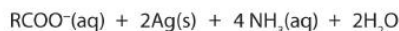
The ease of oxidation helps chemists identify aldehydes. A sufficiently mild oxidizing agent can distinguish aldehydes not only from ketones but also from alcohols. Tollens' reagent, for example, is an alkaline solution of silver (Ag⁺) ion complexed with ammonia (NH₃), which keeps the Ag⁺ ion in solution.



When Tollens' reagent oxidizes an aldehyde, the Ag⁺ ion is reduced to free silver (Ag).



An aldehyde



Free silver

Deposited on a clean glass surface, the silver produces a mirror (Figure 15.3.1). Ordinary ketones do not react with Tollens' reagent.



Figure 15.3.1: Aldehyde Reactions. A reaction related to the Tollens' reaction is often used to silver mirrors. These ornaments were silvered by such a reaction. Glucose, a simple sugar with an aldehyde functional group, is used as the reducing agent. Source: Photo courtesy of Krebs Glas Lauscha, commons.wikimedia.org/wiki/File:Silvering.jpg.

Although ketones resist oxidation by ordinary laboratory oxidizing agents, they undergo combustion, as do aldehydes.

Summary

The polar carbon-to-oxygen double bond causes aldehydes and ketones to have higher boiling points than those of ethers and alkanes of similar molar masses but lower than those of comparable alcohols that engage in intermolecular hydrogen bonding. Aldehydes are readily oxidized to carboxylic acids, whereas ketones resist oxidation.

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15.4: Some Common Aldehydes and Ketones

Learning Objectives

- Objective 1
- Objective 2

Formaldehyde has an irritating odor. Because of its reactivity, it is difficult to handle in the gaseous state. For many uses, it is therefore dissolved in water and sold as a 37% to 40% aqueous solution called *formalin*. Formaldehyde denatures proteins, rendering them insoluble in water and resistant to bacterial decay. For this reason, formalin is used in embalming solutions and in preserving biological specimens.

Aldehydes are the active components in many other familiar substances. Large quantities of formaldehyde are used to make phenol-formaldehyde resins for gluing the wood sheets in plywood and as adhesives in other building materials. Sometimes the formaldehyde escapes from the materials and causes health problems in some people. While some people seem unaffected, others experience coughing, wheezing, eye irritation, and other symptoms.

The odor of green leaves is due in part to a carbonyl compound, cis-3-hexenal, which with related compounds is used to impart a “green” herbal odor to shampoos and other products.

Acetaldehyde is an extremely volatile, colorless liquid. It is a starting material for the preparation of many other organic compounds. Acetaldehyde is formed as a metabolite in the fermentation of sugars and in the detoxification of alcohol in the liver. Aldehydes are the active components of many other familiar materials (Figure 15.4.2).

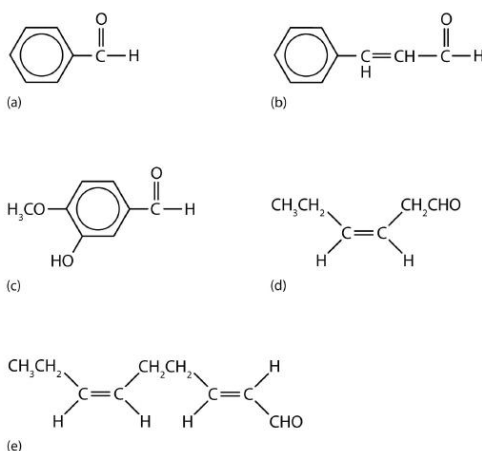


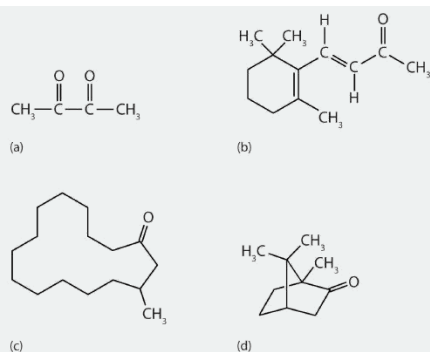
Figure 15.4.2 Some Interesting Aldehydes. (a) Benzaldehyde is an oil found in almonds; (b) cinnamaldehyde is oil of cinnamon; (c) vanillin gives vanilla its flavor; (d) *cis*-3-hexenal provides an herbal odor; and (e) *trans*-2-*cis*-6-nonadienal gives a cucumber odor.

Acetone is the simplest and most important ketone. Because it is miscible with water as well as with most organic solvents, its chief use is as an industrial solvent (for example, for paints and lacquers). It is also the chief ingredient in some brands of nail polish remover.

To Your Health: Acetone in Blood, Urine, and Breath

Acetone is formed in the human body as a by-product of lipid metabolism. Normally, acetone does not accumulate to an appreciable extent because it is oxidized to carbon dioxide and water. The normal concentration of acetone in the human body is less than 1 mg/100 mL of blood. In certain disease states, such as uncontrolled diabetes mellitus, the acetone concentration rises to higher levels. It is then excreted in the urine, where it is easily detected. In severe cases, its odor can be noted on the breath.

Ketones are also the active components of other familiar substances, some of which are noted in the accompanying figure.



Some ketones have interesting properties: (a) Butter flavoring comes from 2,3-butanedione; (b) β -ionone is responsible for the odor of violets; (c) muscone is musk oil, an ingredient in perfumes; and (d) camphor is used in some insect repellents.

Certain steroid hormones have the ketone functional group as a part of their structure. Two examples are progesterone, a hormone secreted by the ovaries that stimulates the growth of cells in the uterine wall and prepares it for attachment of a fertilized egg, and testosterone, the main male sex hormone. These and other sex hormones affect our development and our lives in fundamental ways.

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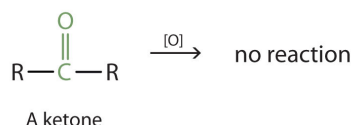
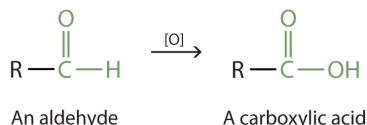
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15.5: Oxidation of Aldehydes

Learning Objectives

- Objective 1
- Objective 2
-

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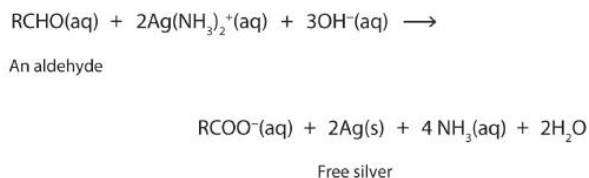
The aldehydes are, in fact, among the most easily oxidized of organic compounds. They are oxidized by oxygen (O_2) in air to carboxylic acids.



The ease of oxidation helps chemists identify aldehydes. A sufficiently mild oxidizing agent can distinguish aldehydes not only from ketones but also from alcohols. Tollens' reagent, for example, is an alkaline solution of silver (Ag^+) ion complexed with ammonia (NH_3), which keeps the Ag^+ ion in solution.



When Tollens' reagent oxidizes an aldehyde, the Ag^+ ion is reduced to free silver (Ag).



Deposited on a clean glass surface, the silver produces a mirror (Figure 15.5.1). Ordinary ketones do not react with Tollens' reagent.

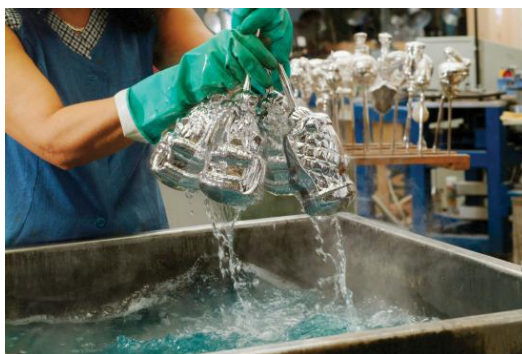


Figure 15.5.1: Aldehyde Reactions. A reaction related to the Tollens' reaction is often used to silver mirrors. These ornaments were silvered by such a reaction. Glucose, a simple sugar with an aldehyde functional group, is used as the reducing agent. Source: Photo courtesy of Krebs Glas Lauscha, commons.wikimedia.org/wiki/File:Silvering.jpg.

Although ketones resist oxidation by ordinary laboratory oxidizing agents, they undergo combustion, as do aldehydes.

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15.6: Reduction of Aldehydes and Ketones



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15.7: Addition of Alcohols - Hemiacetals and Acetals



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