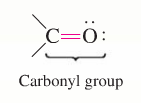
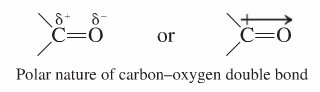
**Chapter 15: Aldehyde and Ketones**

In this chapter, we discuss the hydrocarbon derivatives that contain the element oxygen directly with a carbon-oxygen double bond (carbonyl group). In last chapter, we discussed the functional groups (alcohols phenols, and ethers) have the common feature of carbon-oxygen single bonds. Carbon=oxygen double bonds are also possible in hydrocarbon derivatives. We will now consider the simplest types of compounds that contain this structural feature: aldehydes and ketones.

**15.1 The Carbonyl Group**

Both aldehydes and ketones contain a carbonyl functional group. A carbonyl group is an carbon atom double-bonded to an oxygen atom. The structural representation for a carbonyl group is

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Carbon-oxygen (C=O) and carbon-carbon (C=C) double bonds differ in a major way. A carbon oxygen double bond is more **polar**, and a carbon-carbon single bond is less polar. The electronegativity (Section 5.9) of oxygen (3.5) is much greater than that of carbon (2.5). Hence the carbon-oxygen double bond has more electrons and is more polarized, the oxygen atom acquiring a fraction of negative charge and the carbon atom positive charge as shown in figure above.

**15.2 Compounds Containing a Carbonyl Group**

**Aldehydes:** Carbonyl is attached to at least one **H atom** in aldehydes

**Ketones:** Carbonyl is directly attached with **two carbon atoms** in ketones

**Carboxylic acids:** carbonyl carbon atom bonded to a **hydroxyl group(-OH)**.

**Esters:** carbonyl carbon atom bonded to an **oxygen atom with a alkyl group (-OR).**

**Amide:** carbonyl carbon atom bonded to a **nitrogen atom (-NH2 or -NHR)**

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| --- | --- |
| Aldehydes  Carbon chain on one side of carbonyl and hydrogen on the other | Ketones  Carbon chain on both sides of the carbonyl |
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| **Other Carbonyl Derivatives** | |
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|  |  |

**15.3 The Aldehyde and Ketone Funcitonal Groups**

**Common names of simple aldehydes and ketones**

**Aldehydes:**

Formaldehyde: H**CHO**

    Acetaldehyde:                       CH3**CHO**

    Propionaldehyde:             CH3CH2**CHO**

    Butyraldehyde:           CH3CH2CH2**CHO**

Valeraldehyde:      CH3CH2CH2CH2**CHO**

**Ketones:**

**Acetone:**CH3**CO**CH3

Methyl ethyl ketoneCH3CH2**CO**CH3

Butyl propyl ketoneCH3CH2CH2CH2**CO**CH2CH2CH3

**15.4 Nomenclature for Aldehydes**

Rule 1: Select as the parent carbon chain the longest carbon chain that includes the carbon atom of the carbonyl group.

Rule 2: Name the parent chain by changing the “-e” ending of the corresponding alkane name to “-one.”

Rule 3: Number the carbon chain such that the carbonyl carbon atom receives the lowest possible number. The position of the carbonyl carbon atom is noted by placing a number immediately before the name of the parent chain.

Rule 4: Determine the identity and location of any substituents, and append this information to the front of the parent chain name.

Rule 5: Cyclic ketones are named by assigning the number 1 to the carbon atom of the carbonyl group. The ring is then numbered to give the lowest number(s) to the atom(s) bearing substituents.

**Aldehydes: -al** as suffix

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**Give the condensed structures of following aldehydes:**

|  |
| --- |
| **Aldehydes:**   Ethanal (acetaldehyde)   3-hydroxybutanal (aldol)   3-bromo-5-methylhexanal   1-bromo-5-methyl-3-heptanone |

**15.5 Nomenclature for Ketones**

**Ketones**: -**one** as suffix

**Aromatic ketones**

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**Give the condensed structures of following ketones:**

**Ketones:** (IUPAC/Common)   
propanal (propionaldehyde)    
2-butanone (methylethylketone)    
4,4-dimethyl-2-pentanone    
cyclopentanone    
4-hydroxy-2-cylohexenone

**15.6 Isomerism for Aldehydes and Ketones**

Constitutional isomers exist for aldehydes and ketones

Isomers between aldehydes and ketones are called functional group isomers

Two types of isomers:

* + Skeletal isomers: arrangements of atoms in space is different.
  + Positional isomers: Position of the functional group is different.



**Skeletal isomers**

**Positional isomers**

**The keto and enol forms of aldehydes and ketones**   
Aldehydes and ketones exists in two different isomers also called **tautomers**. Regular carbonyl form of the aldehyde or the ketone is called ***keto form*** and the -OH containing form is called ***enol from***.

 In biological systems keto form of aldehyde sugars (aldoses) are converted to ketone sugars (ketoses) via enediol (enol) form as shown below. Therefore D-fructose which is a ketone or keto sugar (ketose) will give a positive test for Benedict's test because of the ability of ketoses to get converted to aldoses (aldehydes).

**15.7 Selected Common Aldehydes and Ketones**

**Methanal or formaldehyde:**

**structure of fomaldehyde**

Fomalin 40% water solution of formaldehyde has been widely used a preservative for biological specimens.  Formaldehyde is the simplest aldehyde. It is manufactured by oxidizing methanol with air over a metal catalyst in a temperature range of 400-650degrees Celsius. The catalyst can be copper, silver, or molybdeum alloy.



**Ethanal or acetaldehyde:**

Acetaldehyde (common name) also called Ethanal (IUPAC) (CH3CHO), an aldehyde used as a starting material in the synthesis of acetic acid, *n*-butyl alcohol, ethyl acetate, and other chemical compounds. It is manufactured by the oxidation of ethyl alcohol and by the hydration reaction of acetylene. Pure **acetaldehyde** is a colorless, flammable liquid**.**

**2-Propanone or acetone:**

Acetone also called 2-propanone, or dimethyl ketone  (CH3**CO**CH3), organic solvent of industrial and chemical significance, the simplest and most important of the aliphatic (fat-derived) ketones. Pure acetone is a colourless, somewhat  aromatic, flammable, mobile liquid that boils at 56 C. It is also used as nail polish.

**2-Butanone or methyl ethyl ketone:**   
 Important industrial solvent.

**Oil of almonds or benzaldehyde:**

 Found in almond nuts.

**Oil of Cinnamon or cinnamaldehyde:**

Found in cinnamon.

**Berry Flavoring a-Demascone:**

Found in berry.

**Oil of vanilla beans or vanillin:**

Found in vanilla beans.

**Mushroom flavoring or 2-octanone:**

Used as mushroom flavoring.

**Oil of lemongrass or citral:**

Found in lemon grass.

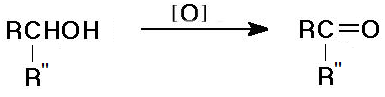
**15.8 Physical Properties of Aldehydes and Ketones**

**15.9 Preparation of Aldehydes and Ketones**

**Preapration of aldehydes:**   
Partial oxidation of primary alcohols with H2CrO4:

**(primary alcohol)          ----                 (aldehyde)**

**Preparation of ketones:**   
Oxidation of secondary alcohols with KMnO4, H2CrO4



**(Secondary alcohol)          ----                 (ketone)**

**Tertiary alcohols doesn't undergo oxidation:**

**(Tertiary alcohols)          ----                 (no reaction)**

**15.10 Oxidation and Reduction of Aldehydes and Ketones**

Aldehyde are readily oxidized to corresponding  carboxylic acids  by number of different oxidizing agents.  The symbol [O] is used to indicate the oxidation process.   
**Benedict's Test for aldehydes:**

  Aldehyde loses an e- (aldehyde is oxidized to an acid)  Cu2+ gains an e- (Cu2+ is reduced to Cu+)

|  |
| --- |
| **Oxidizing Agents and Reducing Agents in the Benedict's Test** |
| Oxidation = loss of an e-   Reduction = gain of an e- |
| The aldehyde is a reducing agent.   The aldehyde is oxidized, but it's oxidation facilitates the reduction of the Cu2+. |
| The Cu2+ is  an oxidizing agent.   The Cu2+ is reduced, but it's reduction facilitates the oxidation of the aldehyde. |
| The travel agent does not travel, but the travel agent facilitates the travel of someone else. |

**Glucose** is an aldehyde sugar which show positive test for the Benedict's test. This test have been used in old days to detect excess bolld sugsr in diabetic patients.

**Tollen's Test:**

A basic Ag(NH3)2+ in aqueous ammonia reduces  to metallic silver (mirror) with aldehyde oxidized to carboxylic acid.

The commercial manufacture of silver mirrors uses a similar process.

**Reduction of carbonyl compounds to alcohols:**   
**Reduction aldehydes and ketones to primary sceondary alcohols** **Reduction Reactions**: Aldehyde and ketones are readily reduced to corresponding alcohols by number of different reducing agents. The symbol [H] is used to indicate the reduction process.  One of the methods is **hydrogenation** where H2 in the presence of a catalyst such as Pt rduces the alcohol. The  methods of  reduction include:

Pt(H2) platinum catalyzed **hydrogenation**   
LiAlH4 lithium aluminum hydride   
NaBH4 (sodium borohydride)

**Reduction of aldehydes:**

**(aldehyde)     ----   (primary alcohol)**

**Reduction of ketones:**

**(Secondary alcohol)          ----                 (ketone)**

**15.11 Reaction of Aldehydes and Ketones with Alcohols**

**Addition reactions to carbonyl double bond in aldehydes and ketones:**

**Hemiacetal and hemiketal formation**

**Hemiacetals**

**Hemiketals**

ketone  + 1st alcohol  ---  hemiketal

**Acetals, and Ketals.**   
    
In biological systems sugars which are complex aldehydes and ketones are found in one of these forms: **hemiacetals,  and hemiketals or acetals and ketals.**

**Cyanohydrin formation**

**Hydrate formation**

**Aldol condensation reactions**   
Aldol condensation is a reaction in which aldehydes  or ketones react to form larger molecules. In biological systems this reaction is catalysed by an enzyme named aldolase.

**aldehyde                aldehyde                                                         aldol**

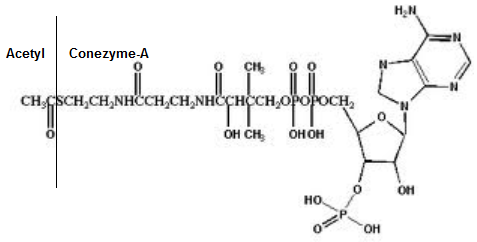
**15.12 Formaldehyde-Based Polymers**

Formaldehyde condense with phenols  under acidic or basic  condition; polymerization gives a network of phenol rings held  together by methylene groups at the ortho and para positions.

This polymer called **bakelite** is a  stiff, three dimensional network with very little solubility in organic solvents and a high resistance to electricity and heat. It is  used in a wide variety of household objects and electrical fixtures.

**15.13 Sulfur-Containing Carbonyl Groups**

Acetyl coenzyme A or acetyl-CoA is an important molecule in metabolism, used in many biochemical reactions. Its main function is to convey the carbon atoms within the acetyl group to the citric acid cycle to be oxidized for energy production. In chemical structure, acetyl-CoA is the thioester between coenzyme A (a thiol) and acetic acid (an acyl group carrier). Acetyl-CoA is produced during the second step of aerobic cellular respiration, pyruvate decarboxylation, which occurs in the matrix of the mitochondria. Acetyl-CoA then enters the citric acid cycle.

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