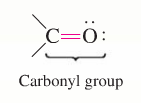
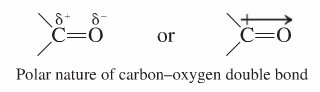
**Chapter 15: Aldehyde and Ketones**

In this chapter, we discuss the hydrocarbon derivatives that contain the element oxygen directly with a double bond. 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 a n atom double-bonded to an oxygen atom. The structural representation for a carbonyl group is

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Carbon-oxygen and carbon-carbon double bonds differ in a major way. A carbon oxygen double bond is **polar**, and a carbon-carbon double bond is nonpolar. The electronegativity (Section 5.9) of oxygen (3.5) is much greater than that of carbon (2.5). Hence the carbon-oxygen double bond is 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**.

**Esters:** carbonyl carbon atom bonded to an **oxygen atom**

**Amide:** carbonyl carbon atom bonded to a **nitrogen atom**

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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:**

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| --- |
| **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:**    
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.



**The keto and enol forms of aldehydes and ketones**   
Aldehydes and ketones exsists 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) froms 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 also called Ethanal (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 of acetylene. Pure **acetaldehyde** is a colourless, 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 idustrial sovent.

**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.

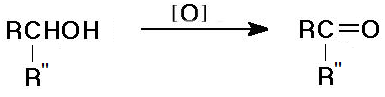
**15.8 Physical Properties of Aldehydes and Ketones**

**15.9 Preparation of Aldehydes and Ketones**

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

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

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



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

**Tertiary alcohols doesn't under go 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**