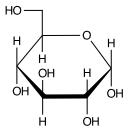
Chem 150, Spring 2015

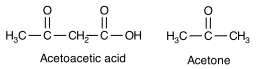
Unit 7 - Aldehydes, Ketones and Redox Reactions

Introductions

- Carbs *vs*. fats and dieting



Glucose
(a carbohydrate)



Ketone Bodies
(derived from fat)

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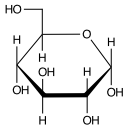

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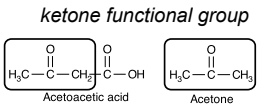
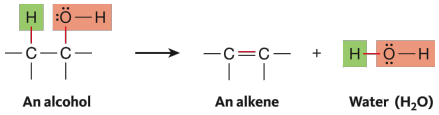


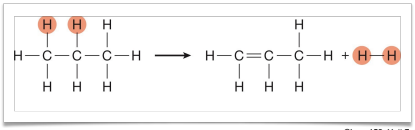
Ketone Bodies
(derived from fat)

11.1 Hydrogenation and Dehydrogenation

- In Unit 6 we saw how an **alkene** can be made from an **alcohol** by the **dehydration** reaction.

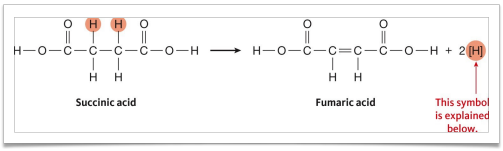


- **Akenes** can also be made from **alkanes** using the dehydrogenation reaction.



11.1 Hydrogenation and Dehydrogenation

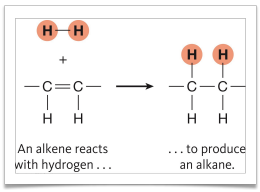
- It is important not to confuse **dehydrogenation** with **dehydration**.
- If a functional group is close to the new alkene double bond in the molecule, the dehydrogenation reaction becomes easier.



(Our bodies always transfer hydrogen atoms to some other molecule when we carry out a dehydrogenation. The symbol [H] can be used to represent hydrogen atoms that are transferred.)

Hydrogenation Reactions

- An alkene can be converted to an alkane by a hydrogenation reaction.



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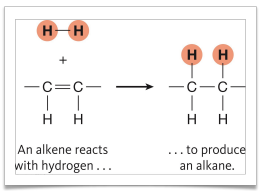

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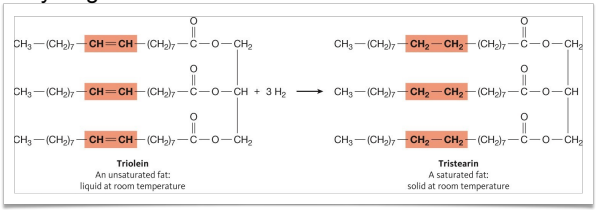

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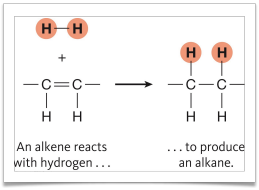


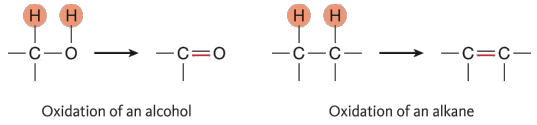
- This reaction is used to convert liquid oils containing unsaturated fats into solid fats containing saturated (hydrogenated fats.

Oxidation and Reduction Reactions

- The dehydrogenation reaction is an example of an oxidation reaction.
  - Any reaction that ***removes* two hydrogen** atoms from an organic compound is an **oxidation**.
- Hydrogenation is an example of a reduction reaction.
  - Any reaction in that ***adds* two hydrogen** atoms to an organic molecule is called a **reduction**.
- Reduction and oxidation reactions are opposites and always occur together. Anytime one compound is oxidized, another must be reduced.

11.2 Oxidation and Reduction Reactions and the Carbonyl Group

- **Alcohols** can also be **oxidized** by **dehydrogenation**
  - In the oxidation of an alcohol two hydrogen atoms are removed and the single bond between the carbon and oxygen is converted to a double bond.
- The C=O group is called a carbonyl group.



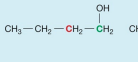
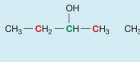
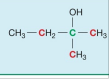
Tertiary Alcohols Cannot Be Oxidized

- To be oxidized, an alcohol must have a hydrogen atom directly bonded to the carbon of the functional group.
- Alcohols are often classified as primary alcohols, secondary alcohols, or tertiary alcohols based on the number of carbon atoms that are adjacent to the functional group.
- Tertiary alcohols cannot be oxidized.

Classification of Alcohols

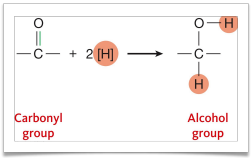
- Alcohols are classified based on the number of carbon attached to the carbon to which the -OH is attached.

TABLE 11.1 Classification of Alcohols

	Methanol	Primary	Secondary	Tertiary
Carbon atoms adjacent to the functional group	None	One	Two	Three
General structure (adjacent carbon atoms are shown in red)				
Example	 (methanol is the only member of this class)			

Carbonyl Groups Can Be Reduced to Alcohols

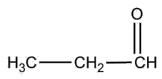
- Compounds that contain carbonyl groups can be reduced just like compounds that contain carbon-carbon double bonds.
  - In this reaction, the double bond becomes a single bond and the carbon and oxygen of the original carbonyl group each gain a hydrogen atom (carbonyl group becomes hydroxyl group).

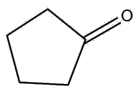


Try It!

Question

Draw the structure of the product obtained when these molecules are reduced.





11.3 The Naming and Properties of Aldehydes and Ketones

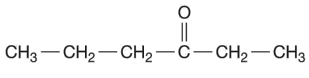
- Aldehydes contain a carbonyl group on an end carbon. The aldehyde group comprises the carbonyl along with the neighboring hydrogen.
  - To name an aldehyde name the carbon chain and replace the *–e* with *–al*.
  - Aldehydes do not need a number to designate where the carbonyl group is because it is automatically carbon number one.
  - Aldehyde groups can be abbreviated to –CHO.

Oxidation of a primary alcohol or methanol . . .

. . . produces an **aldehyde.**

Ketones Contain an Interior Carbonyl Group

- Compounds that have a carbonyl group in the interior of the carbon chain are called ketones. The functional group is called a ketone group.
  - To name a ketone start with the name of the carbon chain and replace the final *–e* with *–one*.
  - A number is given to indicate where the carbonyl is located on the chain. Number from the end that gives the carbonyl carbon the lowest number.



3-Hexanone

Remember to number the chain from the side that is closest to the functional group.

Try It!

Question

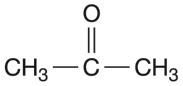
Give the IUPAC name of the molecules shown on the board.

Ketones and Aldehydes with Trivial Names

- Common names are used for some aldehydes and ketones

Formaldehyde
(methanal)

Acetaldehyde
(ethanal)



Acetone

Aldehydes and Ketones have Similar Properties

TABLE 11.2 A Comparison of the Properties of an Alkane, a Ketone, and an Alcohol

	Isobutane (2-Methylpropane)	Acetone (2-Propanone)	Isopropyl Alcohol (2-Propanol)
Structure	$CH_3-CH(CH_3)-CH_3$	$CH_3-C(=O)-CH_3$	$CH_3-CH(OH)-CH_3$
Functional group	None	Ketone	Alcohol
Attraction between molecules	Weakest	Intermediate (the polar carbonyl groups attract each other)	Strongest (the alcohol groups form hydrogen bonds with each other)
Boiling point	−12°C (lowest)	56°C	82°C (highest)
State at room temperature	Gas	Liquid	Liquid

Aldehydes and Ketones have Similar Properties

Question
Which of the following interactions can aldehydes and ketones have among themselves

A. Dispersion interactions
B. Dipole-dipole interactions
C. Hydrogen bonding interactions
D. ionic interactions

(These are the ones that will affect boiling points and melting points)

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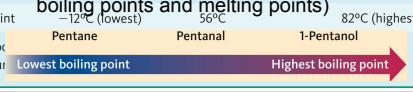

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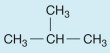
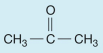
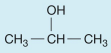
Structure			
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Aldehydes and Ketones have Similar Properties

Question

Which of the following interactions can aldehydes and ketones have with water molecules?

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(These are the ones that will affect solubilities in water)

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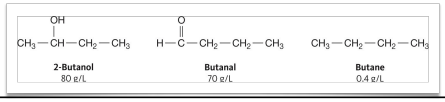

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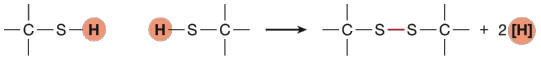
11.4 Other Oxidation and Reduction Reactions

- Thiols can be oxidized to produce a disulfide.
  - This reaction requires two thiol molecules which each lose a hydrogen atom and a new S-S bond forms.
  - The formation and breaking of disulfide groups plays a significant role in protein chemistry.

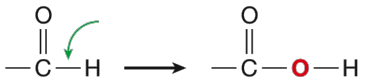


Each thiol group loses its hydrogen atom . . .

. . . and a new bond forms between the two sulfur atoms, giving a **disulfide.**

11.5 Carboxylic Acids

- Adding hydrogen atoms is not the only type of oxidation reaction. The addition of an oxygen atom to a compound is also a type of oxidation.
  - When an aldehyde is oxidized, it gains an oxygen atom and becomes a carboxylic acid.



When an aldehyde is oxidized, it gains an oxygen atom . . .

. . . to form a **carboxylic acid.**

Naming Carboxylic Acids

- Carboxylic acids are named by replacing the *–e* at the end of the alkane name with *–oic* acid.
  - Many carboxylic acids were discovered before the IUPAC naming system, so their trivial names are widely used.
  - The carboxylic acid functional group is often written in condensed form as –COOH or $–CO_2H$.

Formic acid
Methanoic acid

Acetic acid
Ethanoic acid

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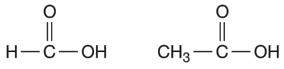
The Latin name for ants is *formica*



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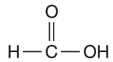

Formic acid
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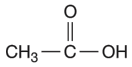
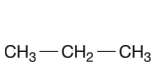


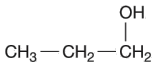
Acetic acid
Ethanoic acid

The Latin name for vinegar is *acetum*

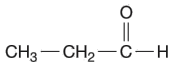
The Physical Properties of Carboxylic Acids



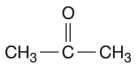
Propane
m.p. = –188°C
b.p. = –42°C



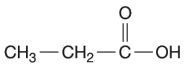
1-Propanol
m.p. = –127°C
b.p. = 97°C



Propanal
m.p. = –81°C
b.p. = 49°C



2-Propanone
m.p. = –94°C
b.p. = 56°C



Propanoic acid
m.p. = –21°C
b.p. = 141°C

The Physical Properties of Carboxylic Acids

Question

Which of the following interactions can carboxylic acids have among themselves

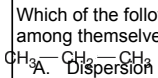
A. Dispersion interactions

B. Dipole-dipole interactions

C. Hydrogen bonding interactions

D. ionic interactions

(These are the ones that will affect boiling points and melting points)



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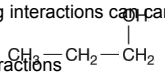

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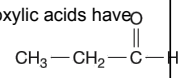

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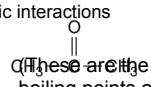

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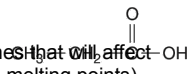
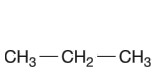
m.p. = –94°C
b.p. = 56°C

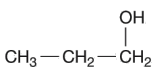


Propanoic acid
m.p. = –21°C
b.p. = 141°C

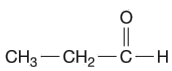
The Physical Properties of Carboxylic Acids



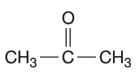
Propane
m.p. = –188°C
b.p. = –42°C



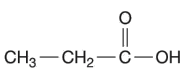
1-Propanol
m.p. = –127°C
b.p. = 97°C



Propanal
m.p. = –81°C
b.p. = 49°C



2-Propanone
m.p. = –94°C
b.p. = 56°C



Propanoic acid
m.p. = –21°C
b.p. = 141°C

The Physical Properties of Carboxylic Acids

Question

Which of the following interactions can carboxylic acids have with water molecules?

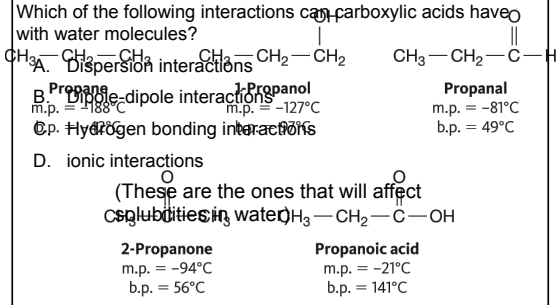
A. Dispersion interactions

B. Dipole-dipole interactions

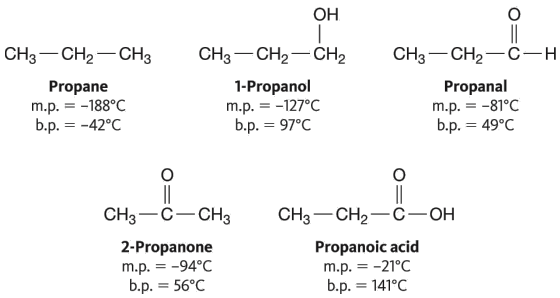
C. Hydrogen bonding interactions

D. ionic interactions

(These are the ones that will affect solubilities in water)



The Physical Properties of Carboxylic Acids



Fatty Acids

- Carboxylic acids can hydrogen bond with water molecules, so carboxylic acids only a few carbon atoms are very soluble in water.
  - The solubility decreases as the carbon skeleton increases.
  - Carboxylic acids containing 10 or more carbon atoms are called *fatty acids*, because they are the building blocks of fats.

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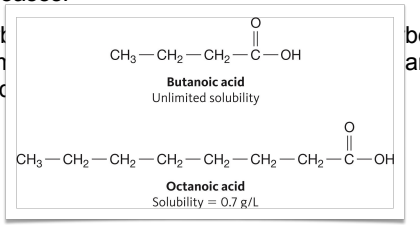

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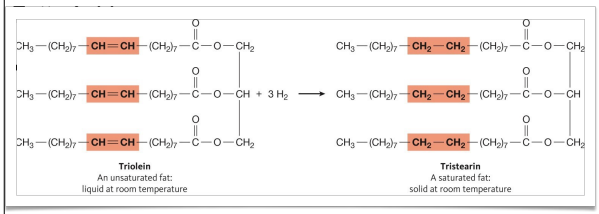

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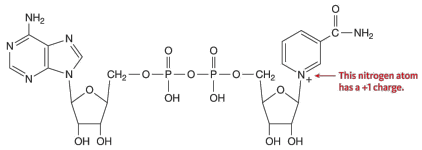
11.6 Biological Oxidations and Reductions: The Redox Coenzymes

- In our bodies, hydrogen atoms are usually donated and removed by a set of organic compounds called the redox coenzymes.
  - The term “redox” is an abbreviation for reduction/oxidation.
  - A coenzyme is an organic compound that helps an enzyme carry out its catalytic function.
  - There are three important redox coenzyme, each of which has its own function: NAD^+, FAD, and $NADP^+$.

NAD^+

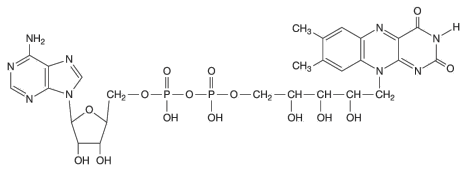
- NAD^+ (*nicotinamide adenine dinucleotide*) is the hydrogen acceptor in most oxidations.
- When it reacts with another organic molecule, it removes two hydrogen atoms from the molecule. One hydrogen atom loses its electron and is released into the solution as H^+. The electron is added to NAD^+, converting it into an electrically neutral molecule called NADH.



The structure of NAD^+, a redox coenzyme

FAD

- FAD (*flavin adenine dinucleotide*) accepts hydrogen atoms when a hydrocarbon is oxidized.
- When FAD reacts with an organic molecule, it removes two hydrogen atoms and both become covalently bonded to FAD forming $FADH_2$.



The structure of FAD, a redox coenzyme

$NADP^+$

- $NADP^+$ (*nicotinamide adenine dinucleotide phosphate*) supplies the hydrogen atoms in reduction reactions.
- The reactant is actually NADPH and the reaction froms $NADP^+$ as the product.
- $NADP^+$ and NAD^+ are similar in structure and their two reactions are essentially opposites.
- NADPH donates hydrogen atoms to another compound, while NAD^+ removes hydrogen atoms from another compound.

The Roles of the Redox Coenzymes

TABLE 11.3 The Roles of the Redox Coenzymes

Coenzyme	Role	Reaction*
NAD^+	NAD^+ accepts the hydrogen atoms that are removed in most types of oxidation reactions.	$NAD^+ + 2\,[H] \rightarrow NADH + H^+$
FAD	FAD accepts the hydrogen atoms that are removed during dehydrogenation reactions ($-CH-CH- \rightarrow -C=C-$).	$FAD + 2\,[H] \rightarrow FADH_2$
NADPH	NADPH supplies the hydrogen atoms that are added during reduction reactions.	$NADPH + H^+ \rightarrow NADP^+ + 2\,[H]$

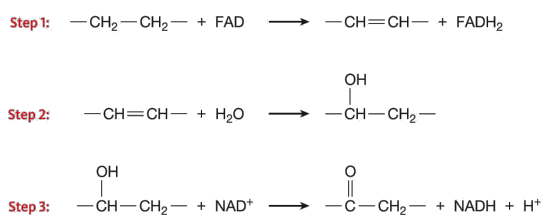
*In the reactions in this table, [H] represents a hydrogen atom that is part of an organic molecule.

11.7 Introduction to Metabolic Pathways

- Our bodies must make and break down many different chemical compounds every day.
- A sequence of reactions that changes one important biological molecule into another is called a metabolic pathway..
- Many of the metabolic pathways our bodies carry out are involved in energy production.
  - Almost all of these energy-producing pathways involve oxidation reactions.

Three-Reaction Sequence

- Many oxidation pathways use the same three-reaction sequence.



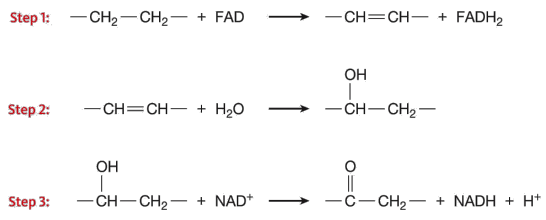
This sequence of reactions is in both fatty acid degradation and the citric acid cycle.

Three-Reaction Sequence

Question

Name the reactions in each of the steps.

- Many oxidation pathways use the same three-reaction sequence.



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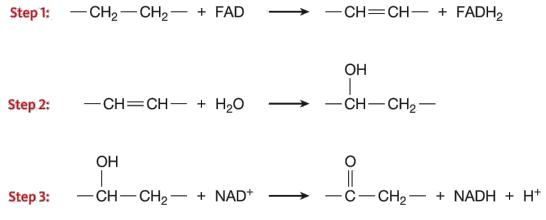
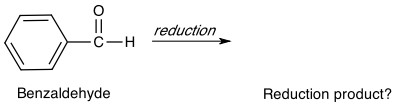


This sequence of reactions is in both fatty acid degradation and the citric acid cycle.

Try It!

Question

If I asked you to draw the structure of the reaction product when benzaldehyde is reduced, why would I mark you wrong if you gave the following answer?



Benzaldehyde Reduction product?

Try It!

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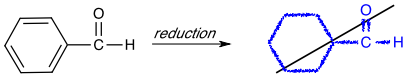

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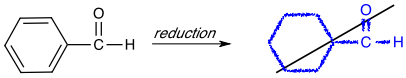

Benzaldehyde Reduction product?

What is the correct answer?

Next Up

- Unit 8: Organic Acids and Bases
  - Chapter 12 in Armstrong
  - Unit 8 Assignments are due on March 19.
  - Deadline for completing the Unit 8 Assignments is March 26.