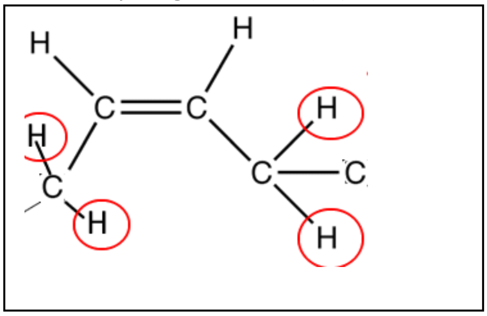
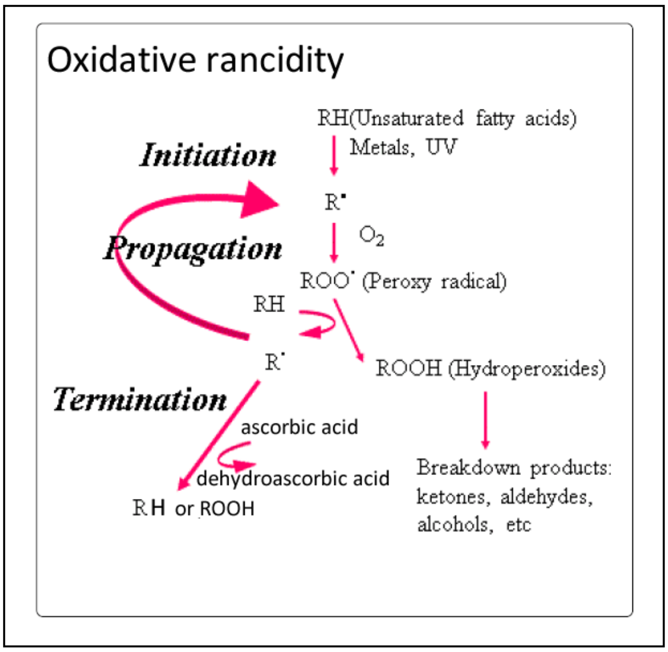
Lesson 3 Rancidity

Introduction

Because of their chemical structure, the presence of double bonds, unsaturated fats and oils are prone to chemical changes, via enzyme action, exposure to light or atmospheric oxygen. One of these chemical processes is known as ***oxidative rancidity*** and produces products with unpleasant smelling compounds. Oxidative rancidity occurs when an unsaturated triglyceride is exposed to oxygen. This causes the unsaturated triglyceride to form compounds such as short chain aldehydes, ketones and saturated fatty acids with an unpleasant smell and taste. The higher the degree of unsaturation, the more double bonds present in the molecule, the more vulnerable the molecule become to oxidative rancidity. This reaction is a free radical chain reaction that involves the removal of a hydrogen radical (H·) from the fatty acid chain followed by a series of reactions with oxygen, produce foul smelling and tasting compounds.



The methylene group, next to a double bond (-CH=CH-**CH_2**-CH=CH-) is particular vulnerable to losing a hydrogen. The lipid radical (R•) formed rapidly reacts with oxygen to form a peroxy radical. The peroxy radical (ROO●) can receive a hydrogen atom to form a lipid hydroperoxide (ROOH) which is relatively stable and exists in significant quantities in many natural fats. The lipid hydroperoxide has no off-flavour but can rapidly break down (particularly in the presence of heat and a metal catalyst) to form rancid flavours.



Lipid oxidation

Phases of lipid oxidation

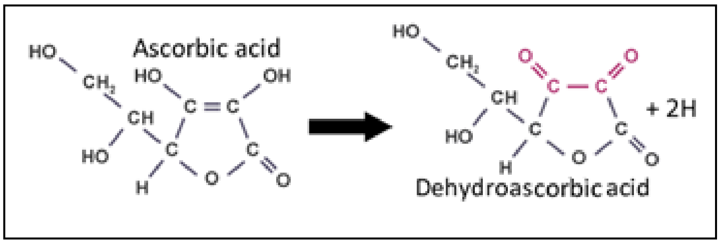
The overall mechanism of lipid oxidation consists of three phases listed below. R· represents a free radical formed by removing a hydrogen from a carbon atom adjacent to a double bond

(1) initiation, the formation of free radicals;
 RH + O_2 → R· + ·OH or R· + O_2 → · + ROO·
(2) propagation, the free-radical chain reactions
 ROO· + RH → R· + ROOH or ROOH → RO· + HO· (RH is any unsaturated fatty acid and ROOH is a hydroperoxide, which decomposes to form compounds responsible for unpleasant odours and flavour)
(3) termination, the formation of non-radical products.
 R· + R· → RR or R· + ROO· → ROOR or ROO· + ROO· → ROOR + O_2

Anti-oxidants

The most common method of preventing oxidative rancidity, is by using compounds known as antioxidants. These compounds do not stop the formation of free radicals but they do prevent their propagation. Vitamin C is used as an antioxidant it is more readily oxidised than fats and oils. When a peroxide radical is formed (ROO·) vitamin C will donate hydrogen atoms to the radical thus preventing its reaction with nearby fat molecules.

Ascorbic acid is converted to the stable compound, dehydroascorbic acid, by losing two hydrogen atoms from the hydroxyl groups present on the ring structure of the molecule.



Apart for antioxidants, other factors that influence the rate of rancidity are:
Temperature: The rate of oxidative rancidity is highly dependent on temperature, the higher the temperature the greater the rate.
Oxygen: Exposure to atmospheric oxygen accelerates the rate of oxidative rancidity, especially in the presence of U.V. light.
Type of fat: The more unsaturated the fat molecule the greater the tendency for oxidative rancidity. Vegetable oils, although unsaturated, are generally more resistant to oxidative rancidity than animal fats because they contain natural antioxidants. Vitamin E is a common antioxidant found in vegetable oils. Fish oils, on the other hand, are highly unsaturated and hence more susceptible to oxidative rancidity.
Metals. Metals such as copper, iron, manganese, and chromium increase rate of fat oxidation.
Water. Enzymes such as lipases are present naturally in fats. These enzymes catalyse hydrolytic reactions that breakdown of fats in the presence of water.

1) Explain how vitamin C acts as an antioxidant.
Vitamin C is used as an antioxidant it is more readily oxidised than fats and oils. When a peroxide radical is formed (ROO·) vitamin C will donate hydrogen atoms to the radical thus preventing its reaction with nearby fat molecules.
2) Fill the gaps below by choosing from the list of words. You may use any word more than once or not at all
Unsaturated fatty acid, saturated, aldehyde, triglyceride, ketone, oxygen, hydrogen
Oxidative rancidity occurs when a ***triglyceride*** is exposed to ***oxygen*** This causes the ***unsaturated fatty acid*** molecule to form short chain compounds such as ***ketones*** , **fatty acids and *aldehyde.***
3) Ascorbic acid is an antioxidant. It is classified as a reducing agent. Explain why it is classified as a reducing agent and how this prevents oxidative rancidity.
An antioxidant is a molecule that prevents the oxidation of certain compounds. Oxidation can lead to the production of free radicals, thus initiating chain reactions that breakdown other molecules. Antioxidants such as ascorbic acid (vitamin C) terminate these chain reactions by donating hydrogen atoms.
4) The unpleasant smells and flavours associated with rancid foods are associated with which group/s of compounds?
a) Ketones, b) oxygen, c) alcohols, d) aldehydes, e) carboxylic acids, f) saturated fatty acids.
a), d) and f).

5) Animal fats are more likely to become rancid than plant oils. Explain why.
Even though plant oils have polyunsaturated fats, which are more prone to undergo oxidative rancidity, they also have natural antioxidants present. Vitamin E, for example is a natural antioxidant and is present in most plant oils.

6) Explain why the softer the fat, the more susceptible it is to oxidative rancidity.
The softer the fat, the more unsaturated are the fatty acids and the more susceptible they are to oxidation and oxidative rancidity.

7) Hydrogenation, is a process where hydrogen atoms are added across a double bond. This process effectively hardens fat and decreases the molecules susceptibility to oxidative rancidity. Explain why hydrogenation hardens the fat and reduces its vulnerability to oxidative rancidity.
The intermolecular bonding between fatty acids molecules is effectively weak dispersion forces. Double bonds tend to kink long fatty acids thus the molecules are unable to pack in tightly together where dispersion forces can take hold. Removing the double bonds causes the molecule to straighten and better pack with other molecules close together where dispersion forces can have a greater impact. Removing double bonds also removes the vulnerability of the molecule to oxygen.

8) Rancidity can be prevented by covering the butter and storing it in a refrigerator.
By covering the butter water and atmospheric oxygen are prevented from coming into contact with the fat. Cold temperatures slow down hydrolysis reactions.

9) When acing as an antioxidant Vit C is converted from ascorbic acid ($C_6H_8O_6$) to dehydroascorbic acid ($C_6H_6O_6$). What type of reaction is this? Explain.
Oxidation reaction. Carbon in ascorbic acid has an oxidation state of *+2/3* and in *dehydroascorbic acid it has an oxidation state of +1.*
It is possible for carbon in an organic compound to have an oxidation state which involves a fraction. The fraction comes about due to the fact that the oxidation number is an average of all the carbon oxidation states that exist in the molecule.

10) It is found that storing meat in plastic containers in cool storage causes them to last longer. Explain why.
Plastic containers remove any traces of metals and keeping the temperature cool slows the rate of reaction.

11) Meat is sometimes packed in containers filled with pressurised nitrogen gas. Explain why.
Nitrogen is an inert gas that displaces oxygen from the container.