Lipid oxidation

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Lipid Oxidation

Lipid oxidation is a complex series of chemical reactions that is initiated when oxygen interacts with unsaturated lipids

- **Nutrition**
  - *Loss of nutrients (e.g., PUFA)*
  - *Formation of toxic reaction products*
- **Food Quality**
  - *Off flavors and aromas*

Oxidation is the main cause of degradation in unsaturated fats. The oxidation level of the oil is of great importance in the food industry. Oxidation leads to rancidity, decreased food quality, and the formation of harmful compounds in food.

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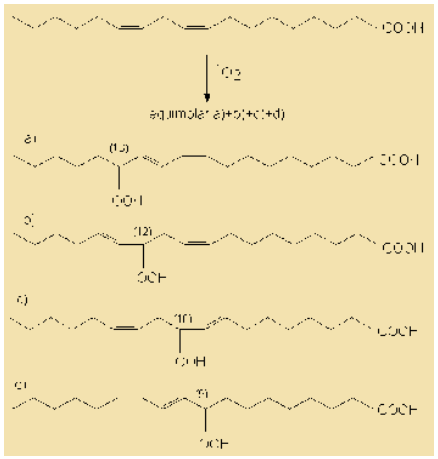
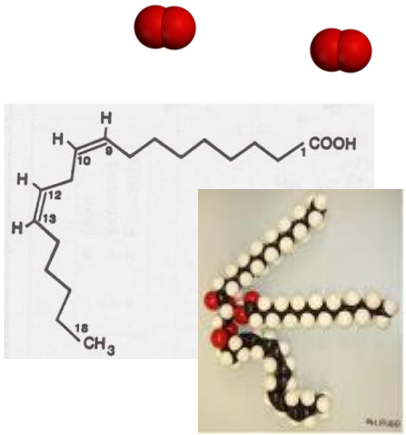


Reactants
(Unsaturated Lipids + O_2)



Primary Reaction Products
(Peroxides and Conjugated Dienes)

Secondary Reaction Products
(Aldehydes, Ketones, Alcohols, Hydrocarbons)

Deterioration in food quality and health

Lipid oxidation

Oxidation can occur in different ways.

1- Autooxidation: It is a 3-stage autocatalytic process that results in rancidity. It is a complex reaction.

In the first step (initiation) H is separated and the alkyl (R *) radical is formed. Generally, there are catalysts such as metals, light, heat and radiation in the environment. The duration of this phase is related to the type of oil, the degree of saturation and the presence of natural antioxidants.

In the second stage (propagation) peroxy radical (ROO *) is rapidly formed from the alkyl radical (R *), in the presence of sufficient oxygen. This reacts with another fatty acid molecule and creates hydroperoxides (ROOH) and new free radicals, initiating a chain reaction.

In the last step (termination) two free radicals interacts to form non-radical species

Auto Oxidation: Mechanism

- A free radical is a highly reactive molecule with an "unpaired" electron that seeks to react with other molecules to find a partner for the unpaired electrons

Major Steps of Lipid Oxidation:

1. **Initiation**

$$X^{\bullet} + RH \rightarrow R^{\bullet} + XH$$

(a) ***Hydrogen abstraction:*** Formation of alkyl radicals (***R***$^{\cdot}$)

2. **Propagation**

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$$

(b) Addition of oxygen to alkyl radical to form **peroxyl radical (*ROO*$^{\cdot}$)**

$$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$$

(c) Reaction of peroxyl radical and unsaturated lipid to form peroxide and alkyl radical

$$ROOH + ROOH \rightarrow RO^{\bullet} + ROO^{\bullet} + H_2O$$

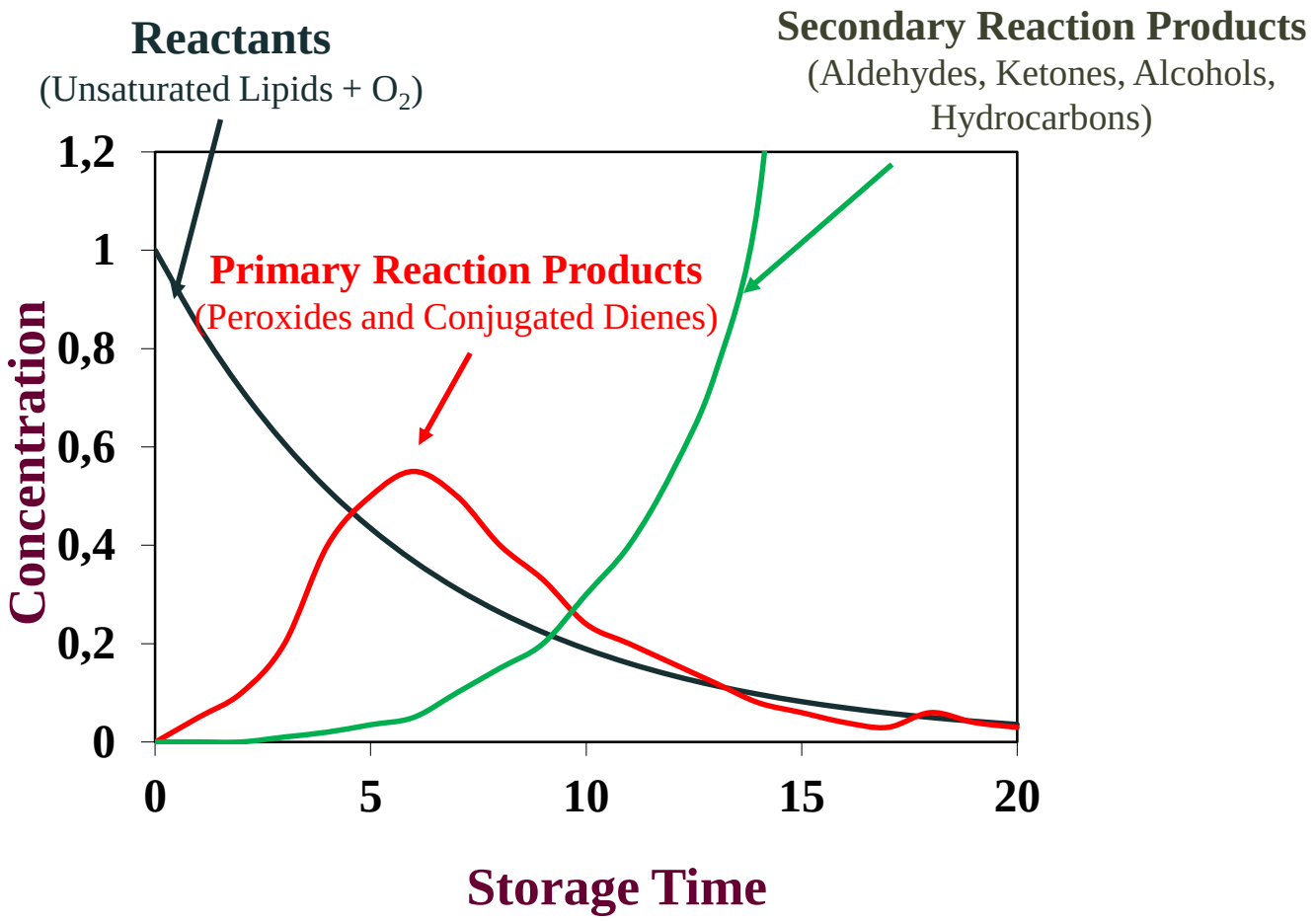
(d) Reaction of 2 peroxides to form further free radicals: **alkoxyl radicals** (*RO*$^{\cdot}$) **& peroxyl radicals (*ROO*$^{\cdot}$)**

3. **Termination**

$$R\cdot, RO\cdot, ROO\cdot \rightarrow \text{stable species}$$

(e) Reactions that lead to formation of stable non-propagating species

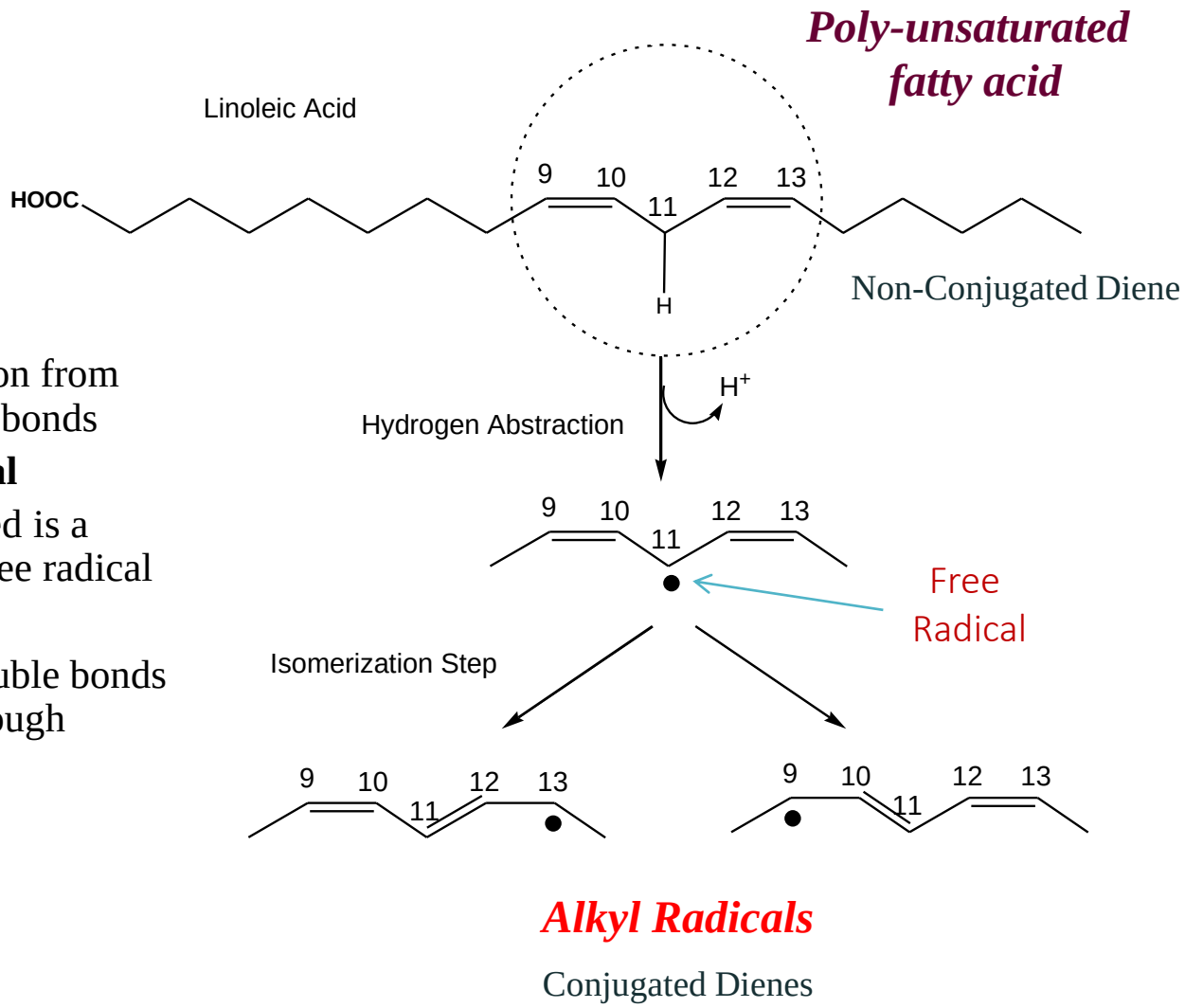
Lipid Oxidation



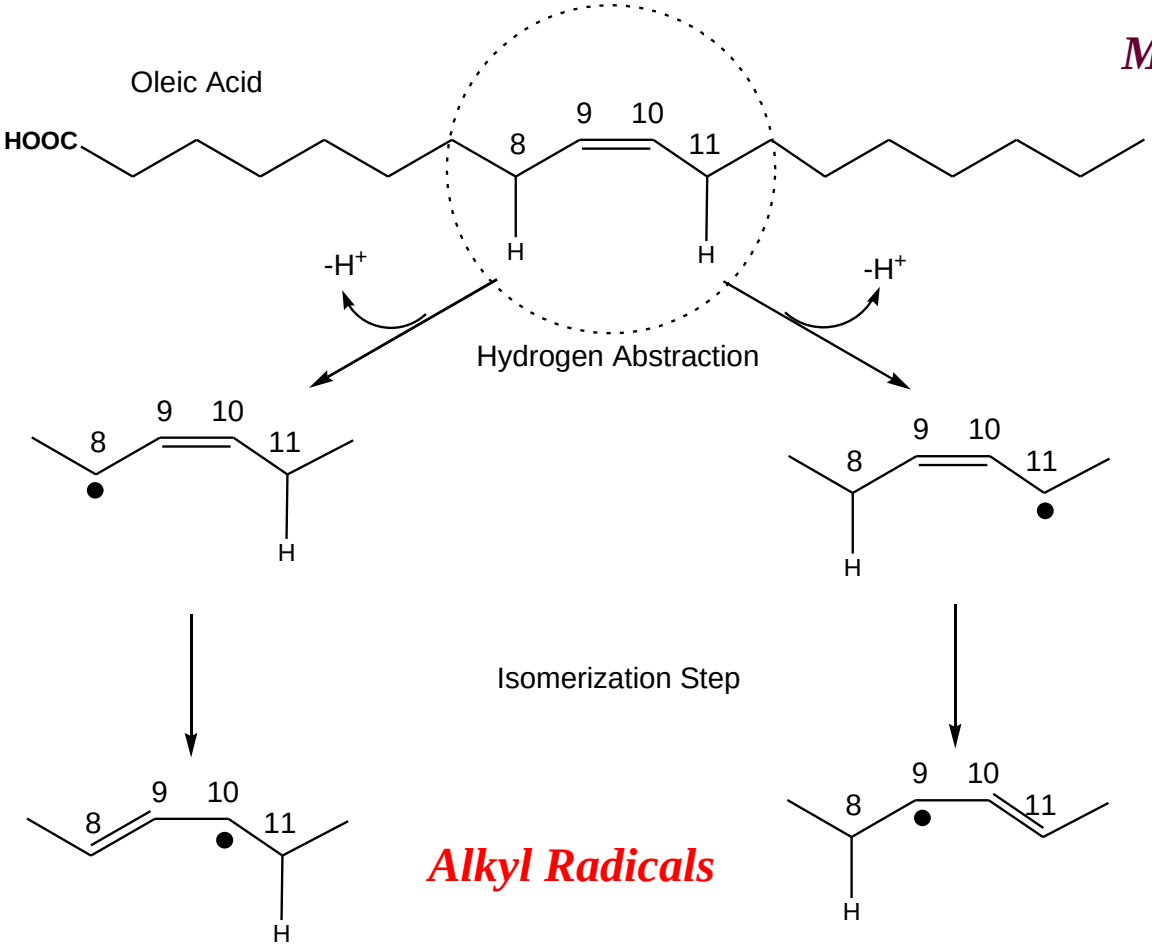
Lipid Oxidation: Initiation

Initiation:

- **(1) Hydrogen abstraction**
  - Removal of hydrogen ion from carbon between double bonds
- **(2) Formation of free radical**
  - The ***alkyl radical*** formed is a relatively low energy free radical
- **(3) Conjugation**
  - The non-conjugated double bonds become conjugated through isomerization



Lipid Oxidation : Initiation



Mono-unsaturated fatty acid

*The type of **alkyl radicals** formed, and the rate of their formation, depends on the structure of the initial fatty acids, especially their degree of unsaturation*

Lipid Oxidation: Propagation

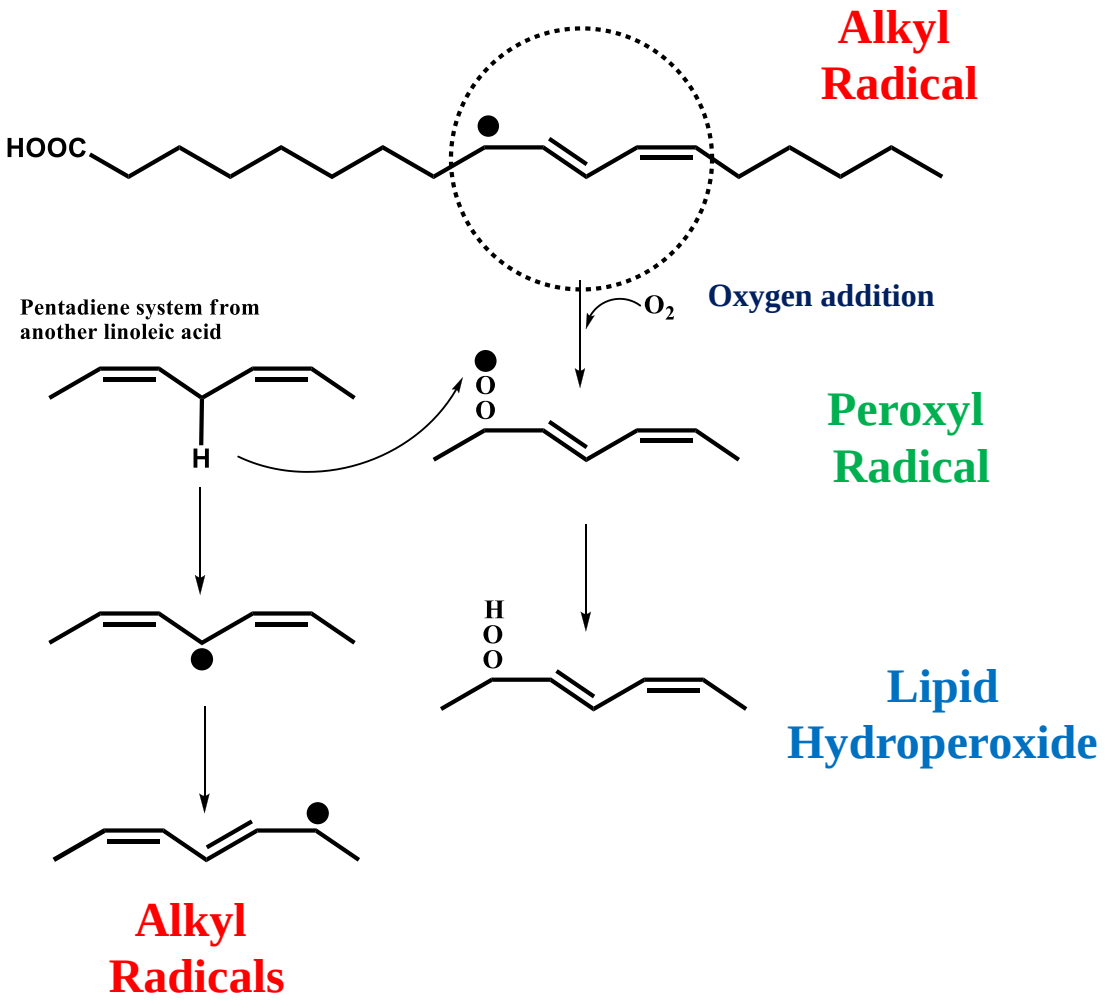
Propagation:

(1) Oxygen addition

- An oxygen molecule reacts with the **alkyl radical** to form a **peroxyl radical**

(2) Hydroperoxide formation

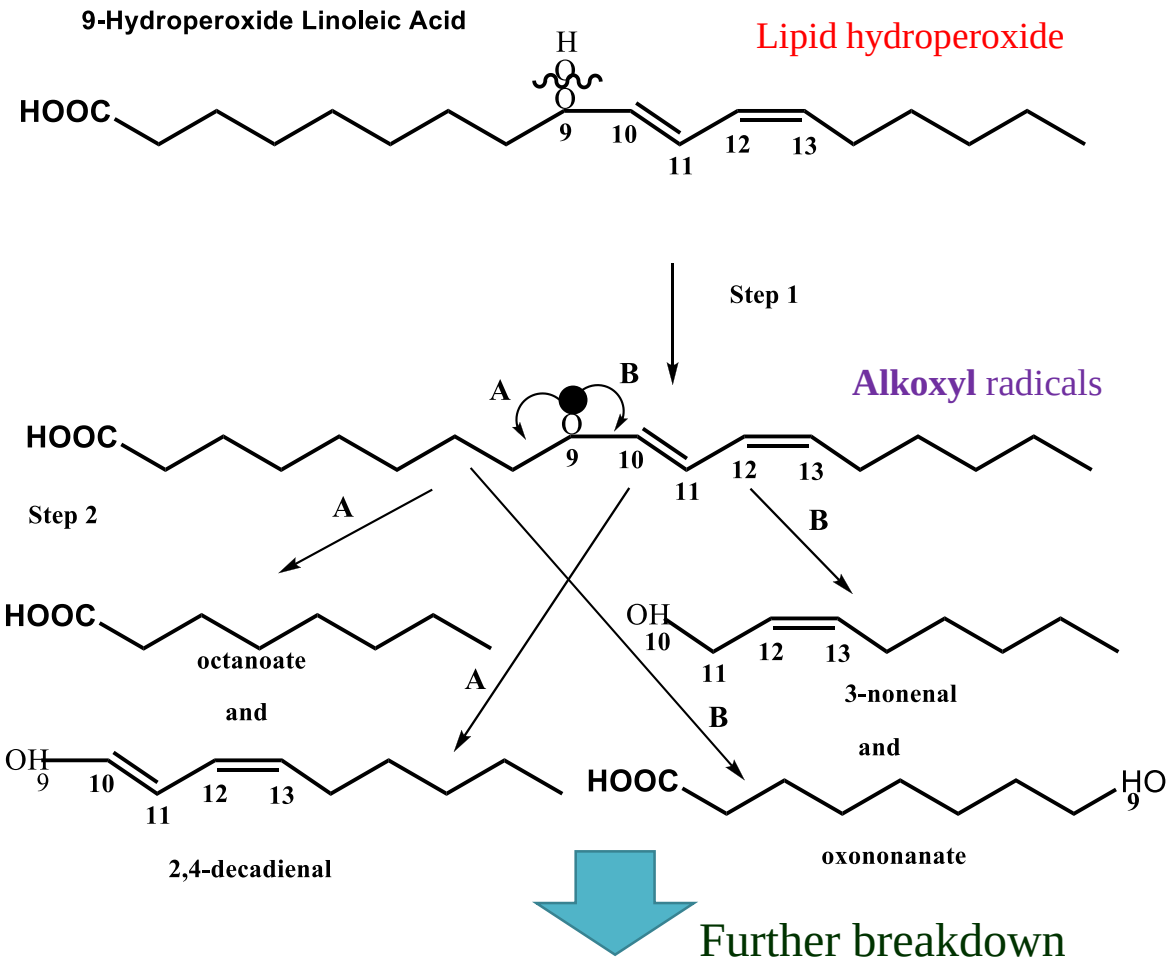
- The **peroxyl radical** is a high energy free radical
- Higher energy allows for abstraction of hydrogen from another unsaturated fatty acid resulting in the formation of a **lipid hydroperoxide** and another **alkyl radical**



Lipid Oxidation: Propagation

β-Scission Reactions

- Breakdown of lipid hydroperoxides to **alkoxyl radicals**
- **Alkoxyl radical** has a very high energy
- High energy of **alkoxyl radical** allows it to steal electron from adjacent covalent bond resulting in cleavage of hydrocarbon chain into various **secondary lipid oxidation products** such as aldehydes, hydrocarbons and ketones

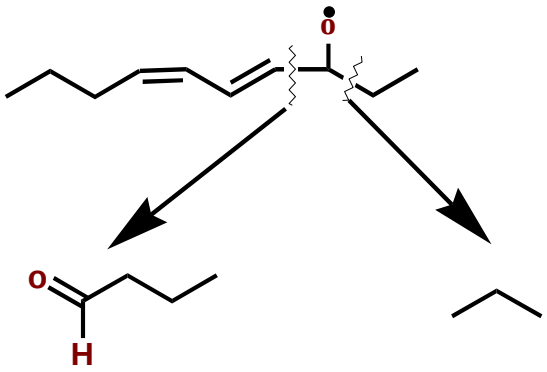


Secondary lipid oxidation products

Lipid Oxidation: Secondary Reaction Products

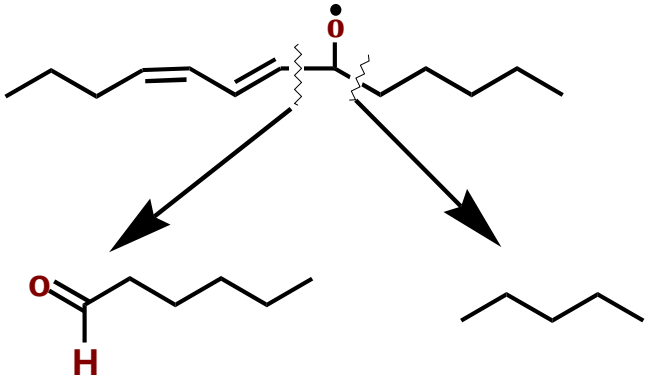
Types of products formed are dependent on fatty acids being oxidized

β -SCISSION OF AN FATTY ACID ω -3



PROPANAL ETHANE

β -SCISSION OF AN FATTY ACID ω -6



HEXANAL PENTANE

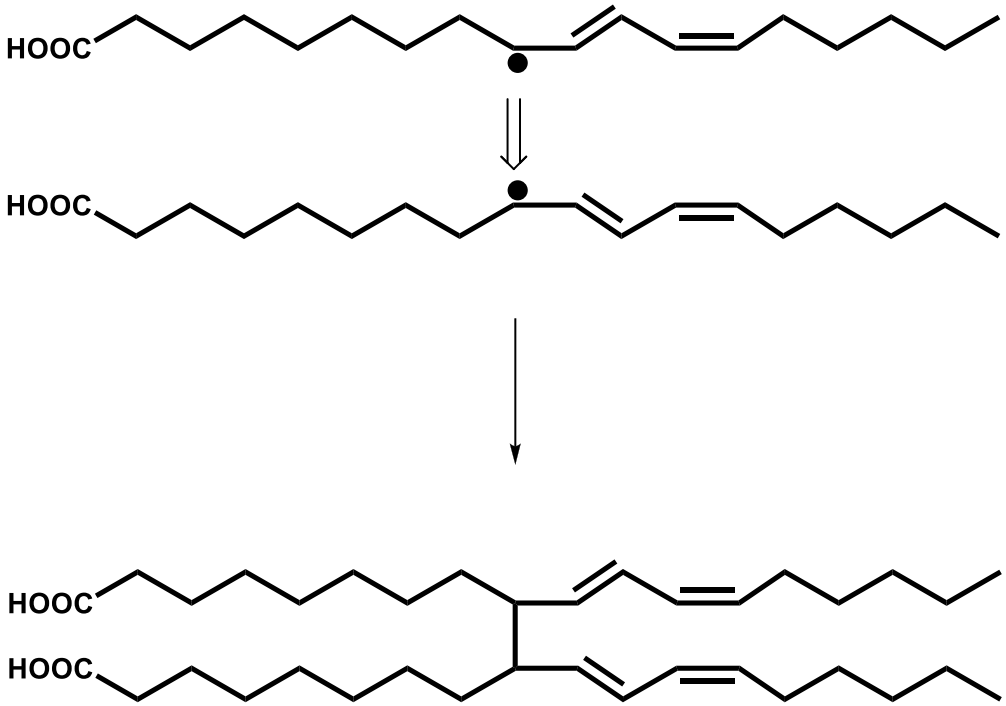
Secondary lipid oxidation products

- Volatile molecules that can cause off flavors and aromas at very low concentrations (ppb).
- Reactive molecules that can react with other food components

Lipid Oxidation: Termination

Termination

- Interaction of two free radicals to form non-radical species
- Not very important in food because food is already rancid at this point



Other ways of oxidation are:

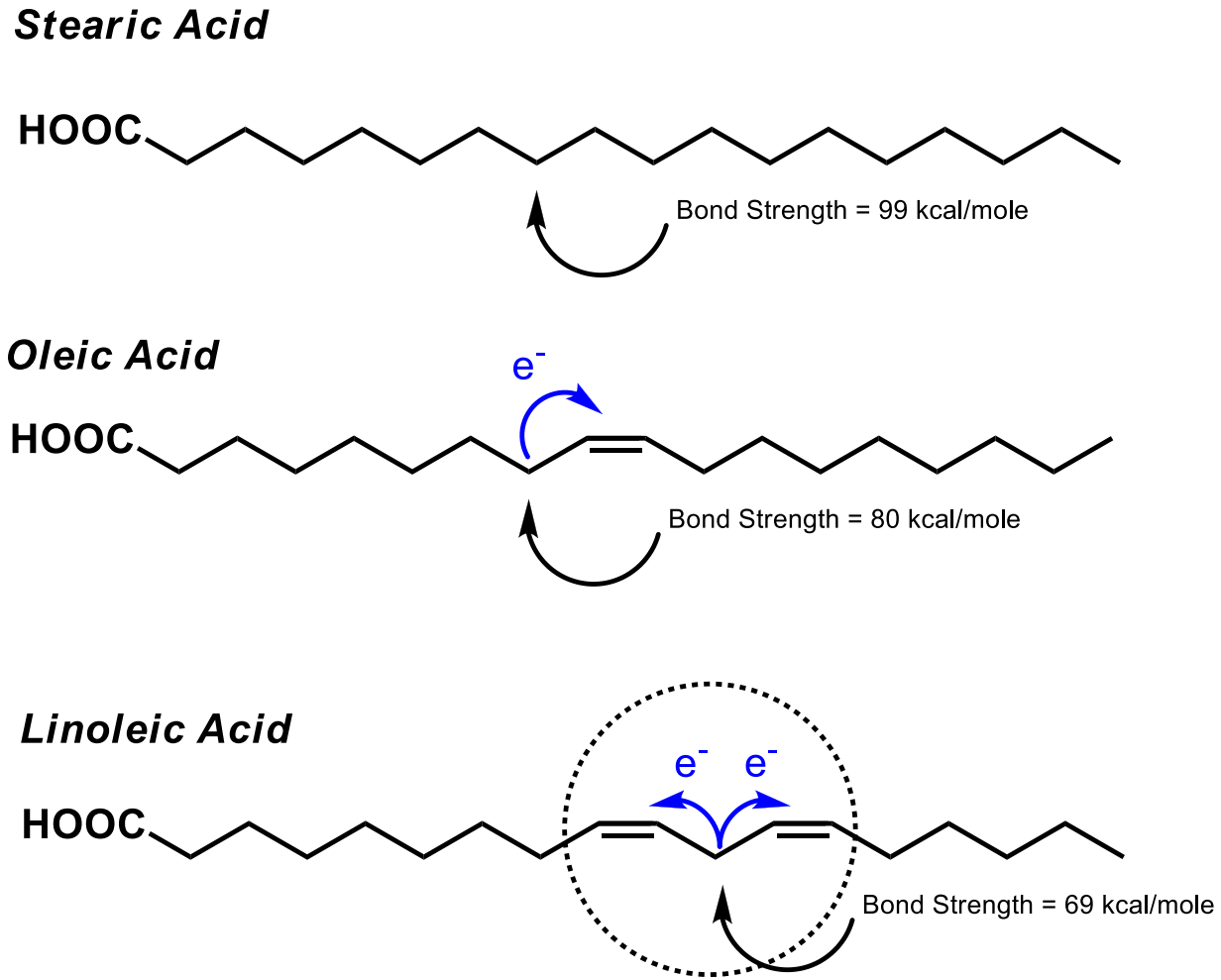
2- Light-catalyzed oxidation (Photooxidation): The reactive oxygen molecule (singlet oxygen) formed by the activation of light reacts with unsaturated fatty acids and hydroperoxides are formed. Unlike autooxidation, it is not a chain reaction, although the products formed are similar to those that occur in autooxidation, it is not the same and is a faster reaction.

3- Oxidation catalyzed by metals: Some metal ions such as cobalt, iron, magnesium and copper initiate the reaction of fatty acids with oxygen. The result is a peroxy radical, which initiates a chain reaction.

4- Oxidation catalyzed by enzymes: The main enzyme is lipoxygenase. The reaction is similar to that in autoxidation. The most preferred substrate is linoleic acid, resulting in hydroperoxides.

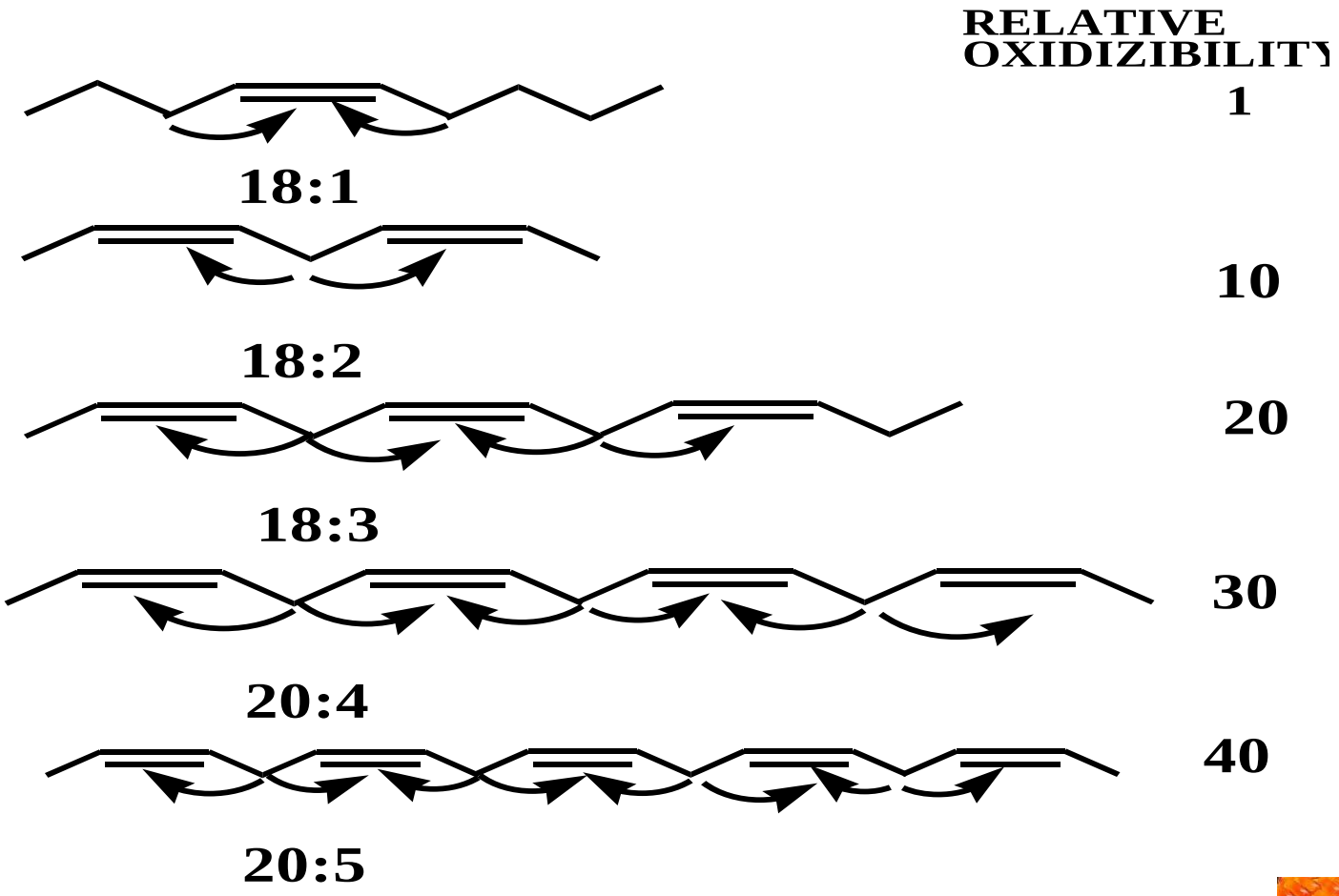
5- Decomposition of Hydroperoxides: Short-chain compounds formed as a result of decomposition of hydroperoxides formed by the above-mentioned means are the main reason for the deterioration of the taste of foods containing fat in their structure. The main compounds formed here are hydrocarbons, alcohols, furans, aldehydes, and ketones. Aliphatic aldehydes are the main reason for unpleasant taste and odor.

Factors Affecting Lipid Oxidation: Lipid Type



The susceptibility of fatty acids to oxidation increases as the number of double bonds increases, since this decreases the strength of the bonds holding hydrogen atoms to carbon atoms

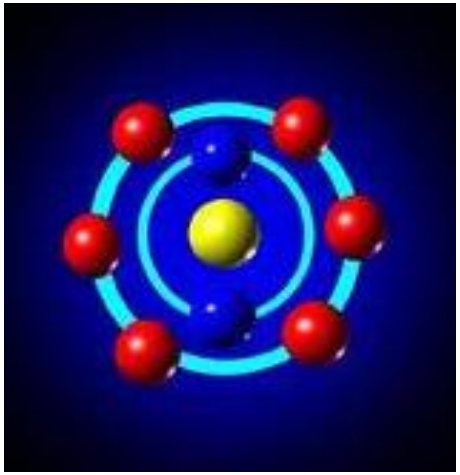
Factors Affecting Lipid Oxidation: Lipid Type



The susceptibility of fatty acids to oxidation increases as the number of double bonds increases

Factors Affecting Lipid Oxidation: Oxygen Concentration

- Oxygen is a bi-radical since it has two *lone pairs* of electrons
- Only very small amounts of oxygen are needed to promote oxidation
- Hence, almost complete removal of oxygen is necessary to stop lipid oxidation (vacuum packing or packing under nitrogen)



Pro-oxidants

A pro-oxidant is a substance that speeds up the rate of lipid oxidation.

Examples:

Transition Metals

Iron, Copper

Heme Proteins

Myoglobin, Hemoglobin

Radiation

Specific Enzymes

Lipoxygense

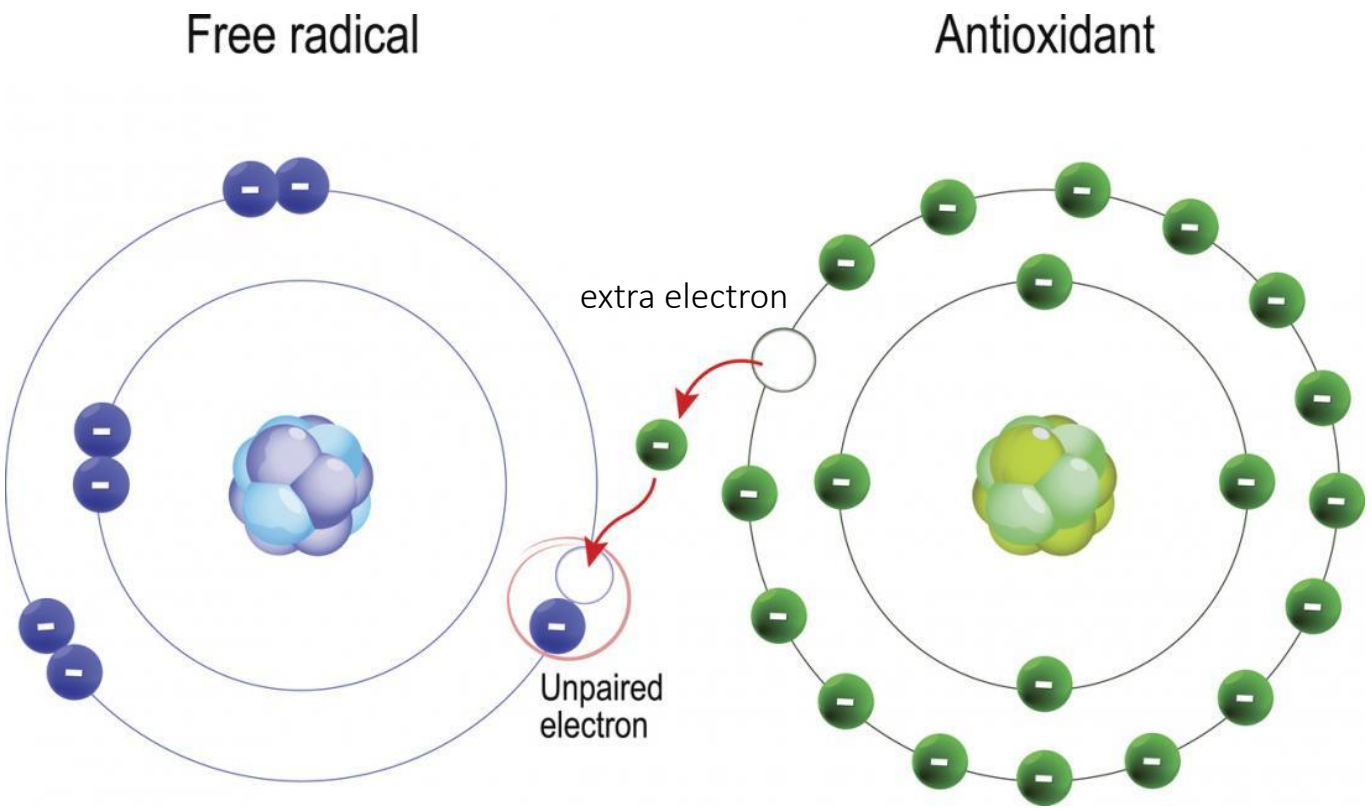
Pro-oxidants work by a number of different physicochemical mechanisms

Antioxidants

An anti-oxidant is a substance that slows down the rate of lipid oxidation. Antioxidants can be classified according to their mechanism of operation (free radical scavengers, metal chelators etc.)

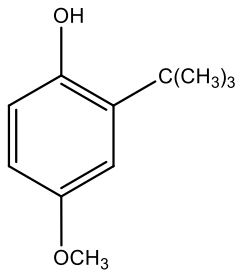
Free radical scavengers

FRS interacts with free radicals.

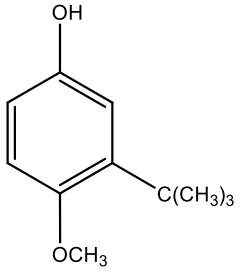


α-tocopherol (Vit. E), ascorbic acid (Vit. C), β carotene (Vit. A), selenium, BHA, BHT, TBHQ, propyl gallate (PG)

Commercially Available Antioxidants: Synthetic Antioxidants

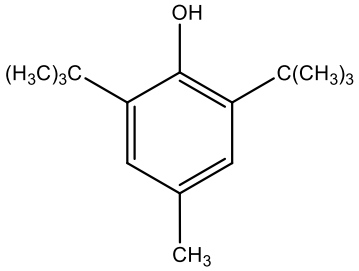


2-BHA

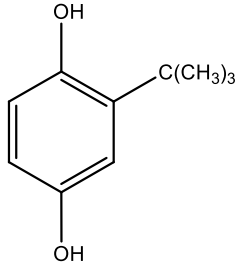


3-BHA

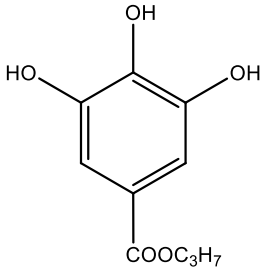
Butylated hydroxyanisole



Butylated hydroxytoluene



Tertiary butylhydroxyquionone

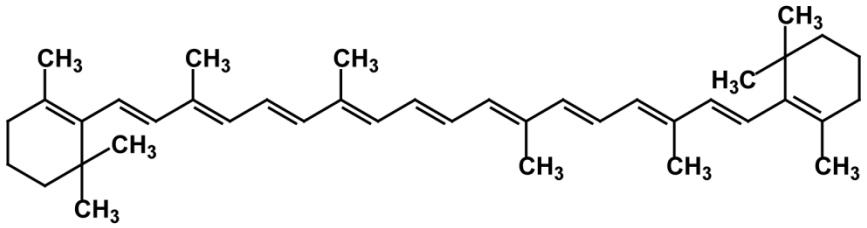


Propyl gallate

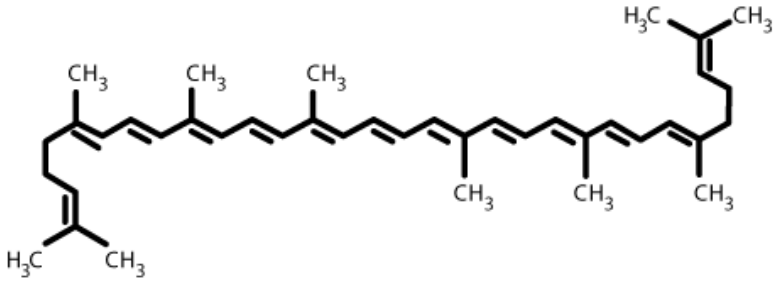
Water Solubility
BHT = BHA < TBHQ < PG

Most limited to 0.02% of fat content

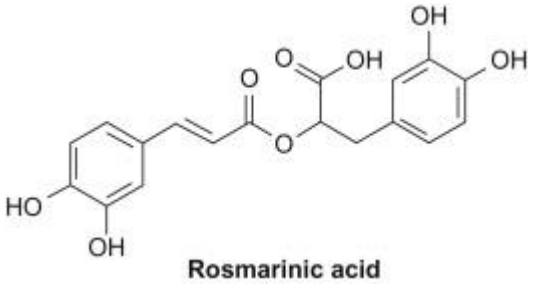
Commercially Available Antioxidants: Natural Antioxidants



β-Carotene



Lycopene



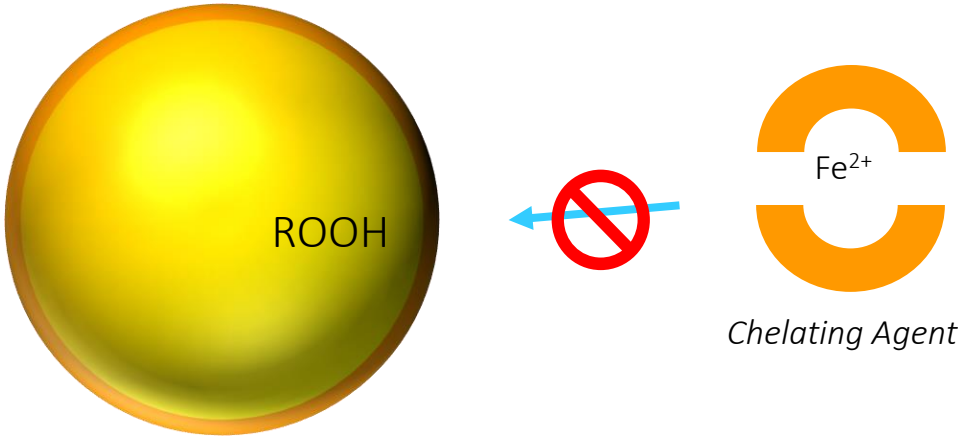
Rosmarinic acid

Grape seed extract

Flavonoids, etc

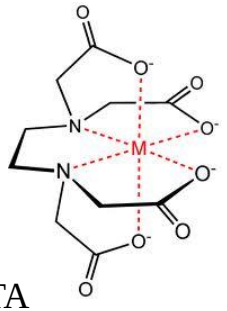
Antioxidants: Chelating Agents

Chelators inhibit the activity of prooxidant metals



Iron can be inactivated by chelating

- Chelating agents (EDTA, organic acids, polyphosphates)
- Proteins (Transferrin, Phosvitin, Lactoferrin, Ferritin)
- Polysaccharides (xanthan)



EDTA

Lipid Oxidation: Factors Affecting

Lipid Type

Rate increases with increasing lipid unsaturation

Oxygen

Rate increases with increasing oxygen concentration

Light

UV-light accelerates the oxidation rate

Heat

High temperatures accelerate the oxidation rate

Pro-oxidants

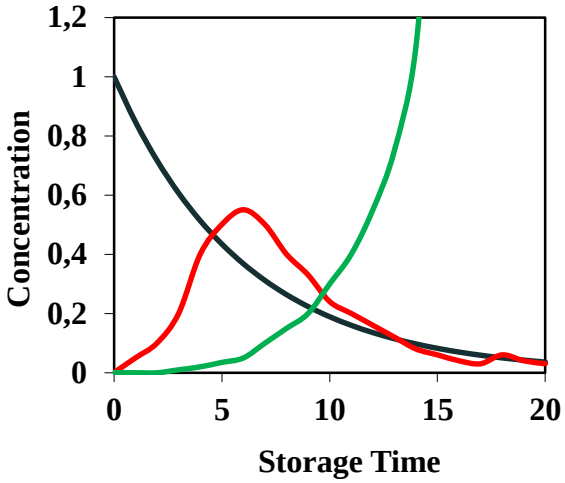
Transition metals, some enzymes and other types of molecules can accelerate the oxidation rate

Anti-oxidants

Various kinds of molecules can act as antioxidants and slow oxidation

Chelating agents

Chelating agents can strongly bind to transition metals and prevent them from accelerating oxidation



Often combine multiple approaches