بِسْمِ ٱللَّهِ ٱلرَّحْمَٰنِ ٱلرَّحِيمِ

رَبِّ اشْرَحْ لِیْ صَدْرِیْ O وَیَسِّرْلِیْ اَمْرِیْ O

وَ ا حْلُلْ عُقْدَةً مِّنْ لِّسَانِیْ O یَفْقَهُوْا قَوْلِیْ O

اے میرے رب! میرا سینہ کھول دے اور میرے لیے میرا کام آسان کر دے اور
میری زبان کی گرہ کھول دے تا کہ لوگ میری بات سمجھ سکیں

رَّبِّ زِدْنِی عِلْمًا

MY LORD! INCREASE ME IN KNOWLEDGE.

FST-311. FOOD BIOCHEMISTRY 3(3-0)

L # 44 - 48. LIPIDS IN FOOD APPLICATION:

LIPID OXIDATION (LO)

B. Sc. (Hons). Food Science and Technology
Semester-V (R+SS)
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RANCIDITY

- RANCIDITY IS THE CONDITION REACHED IN CERTAIN FOODS AS THE LIPID MATERIAL (**FAT**) UNDERGOES OXIDATION REACTIONS PRODUCING ALDEHYDES, HYDROXYL ACIDS, KETA ACIDS, AND OTHER COMPOUNDS WHICH ARE RESPONSIBLE FOR THE ODOR AND OFF-FLAVOR PRODUCING STALE FOODS
- AN OXYGEN ION IS REPLACED WITH A HYDROGEN ION IN THE FATTY ACID
- FOODS THAT ARE HIGH IN LIPIDS AND MIGHT BECOME RANCID INCLUDE POTATO CHIPS, PEANUT BUTTER, CRACKERS, AND OTHERS
- LIGHT, OXYGEN, TRACE ELEMENTS SUCH AS IRON AND ZINC, SALT, WATER, BACTERIA, AND MOLDS ARE FACTORS THAT SPEED UP THE OXIDATION PROCESS

TYPES OF RANCIDITY

- Hydrolytic Rancidity—caused by a breakdown of the fat into glycerol and fatty acid
  - Fatty acids are organic compounds containing carbon, hydrogen, and oxygen that combine with glycerol to make a lipid
  - Glycerol is the storage form of fat in animals
- Oxidative Rancidity—results from oxidation of unsaturated and polyunsaturated fatty acids producing undesirable flavors and odors
  - Oxidation is when a chemical reaction occurs forming oxides by reacting with oxygen in the air.
  - Saturated fatty acids are fatty acid molecules containing no double bonds between carbon atoms—the molecule is "saturated" with hydrogen atoms—found in animal fat
  - Unsaturated (polyunsaturated) fatty acids are fatty acid molecules containing double bonds between carbon atoms—plant oils are unsaturated

RANCIDITY

- The condition reached in certain foods as the lipid material (fat) undergoes oxidation reactions producing aldehydes, hydroxyl acids, keta acids, and other compounds which are responsible for the odor and off-flavor producing stale foods
- Foods high in lipids
  - potato chips
  - peanut butter
  - crackers
- Factors causing rancidity
  - light
  - oxygen
  - trace elements (i.e.—iron, zinc)
  - salt
  - water
  - bacteria
  - mold

(Courtesy, Agricultural Research Service)

LIPID OXIDATION (LO) / RANCIDITY

"LO IS **UNCONTROLLED OXIDATIVE DEGRADATION** OF **LIPIDS** INITIATED BY **FREE RADICALS** (**STEALING ELECTRONS)"** WHICH IS THE FIRST STEP IN THE FORMATION OF SEVERAL SUBSTANCES THAT AFFECTS FOOD PRODUCTS AND INFLUENCE THE **OVERALL QUALITY".**

- **LO** REFERS TO THE **OXIDATIVE** DEGRADATION OF **LIPIDS**
- IT IS THE PROCESS IN WHICH **FREE RADICALS** "**STEAL**" **ELECTRONS** FROM THE LIPIDS

LIPID OXIDATION (LO)

- IT IS THE PROCESS IN WHICH **FREE RADICALS** "**STEAL**" **ELECTRONS** FROM THE LIPIDS IN **CELL MEMBRANES,** RESULTING IN **CELL DAMAGE**
- THIS PROCESS **PROCEEDS** BY A **FREE RADICAL CHAIN REACTION** MECHANISM
- **LO** IS A TERM EXPLAINING DIFFERENT TYPES OF REACTIONS, HAVING BOTH **POSITIVE** AND **NEGATIVE** IMPLICATIONS ON THE HUMAN BODY
- IN THE BODY **LO** IS IMPORTANT FOR SEVERAL PHYSIOLOGICAL REACTIONS, FOR INSTANCE WHEN UTILIZING FATTY ACIDS FOR THE PRODUCTION OF **ENERGY** THROUGH **β-OXIDATION**

LIPID OXIDATION (LO)

- DUE TO OXIDATION, **EDIBLE OILS** CONTAINING **UNSATURATED FATTY ACIDS** ARE OF **MAJOR CONCERN** IN THE FOOD INDUSTRY
- **DEGRADATION** OF **UNSATURATED FATTY ACIDS** BY **OXIDATION** IS DIRECTLY RELATED TO **ECONOMIC**, **NUTRITIONAL**, **FLAVOR**, **SAFETY** AND **STORAGE** **PROBLEMS**
- THERE ARE **TWO MAJOR** OXIDATION REACTIONS WHICH CAN OCCUR IN FOOD STUFF CONTAINING LIPIDS
  - ***AUTO-OXIDATION***
  - ***PHOTO-OXIDATION***
- **AUTO-OXIDATION IS THE MOST COMMON**

LIPID OXIDATION (LO)

AUTO-OXIDATION

- IT OCCURS IN THE PRESENCE OF **O_2** AND IS DESCRIBED AS THE **AUTO-CATALYTIC GENERATION** OF **FREE RADICALS**
- IT IS **INITIATED** WHEN A **H** ATOM IS ABSTRACTED IN THE PRESENCE OF INITIATORS SUCH AS **LIGHT**, **HEAT**, **METALS** OR **OXYGEN**, FORMING A **LIPID RADICAL**, WHICH REACTS WITH **OXYGEN** MAKING A **LIPID PEROXIDE RADICAL**
- THESE **PEROXIDE RADICALS** REACTS WITH A **SECOND LIPID**, YIELDING A **LIPID RADICAL** AND A **HYDROXYPEROXIDE**
- THE REACTION MAY BE **STAGGERED** BY **ANTIOXIDANTS** PRODUCING A COMBINATION OF **RADICAL** SPECIES TO GIVE **NON-RADICAL** AND **NON-PROPAGATING SPECIES**

LIPID OXIDATION (LO)

PHOTO-OXIDATION

- IT OCCURS WHEN **NORMAL TRIPLET OXYGEN** ARE CONVERTED TO **SINGLET OXYGEN** BY THE EXPOSURE OF **UV RADIATION**
- THE **SINGLET OXYGEN INTERACTS** WITH **POLYUNSATURATED FATTY ACIDS** TO FORM **HYDROXYPEROXIDE** WHICH **INITIATE** THE **AUTO-OXIDATION REACTION**

LIPID OXIDATION (LO)

THE OVERALL MECHANISM OF **LO** CONSISTS OF **THREE** PHASES

INITIATION

THE FORMATION OF **FREE** RADICALS

PROPAGATION

THE FREE RADICAL **CHAIN** REACTIONS

&

TERMINATION

THE FORMATION OF **NON-RADICAL** PRODUCTS

LIPID OXIDATION (LO)

INITIATION

$RH + O_2 \rightarrow R^{\cdot} + {}^{\cdot}OH$

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

PROPAGATION

$ROO^{\cdot} + RH \rightarrow R^{\cdot} + ROOH$ (UNSTABLE)

$ROOH \rightarrow RO^{\cdot} + HO^{\cdot}$

TERMINATION

$R^{\cdot} + R^{\cdot} \rightarrow RR$

$R^{\cdot} + ROO^{\cdot} \rightarrow ROOR$

$ROO^{\cdot} + ROO^{\cdot} \rightarrow ROOR + O_2$

LIPID OXIDATION (LO)

WHERE,

- **RH** IS ANY **UNSATURATED FATTY ACID**
- **$R^{\cdot}$** IS A **FREE RADICAL** FORMED BY REMOVING A **LABILE HYDROGEN** FROM A **CARBON** ATOM **ADJACENT** TO A **DOUBLE BOND**
- **ROOH** IS A **HYDROPEROXIDE**, **ONE** OF THE MAJOR **INITIAL OXIDATION** PRODUCTS THAT **DECOMPOSE** TO FORM COMPOUNDS RESPONSIBLE FOR **OFF-FLAVORS** AND **ODORS** **e.g.**
  - ***HEXANAL*** ***(ALDEHYDES)***
  - ***PENTANAL*** ***(ALDEHYDES)***
  - ***MALONALDEHYDE*** ***(ALDEHYDES)***

LIPID OXIDATION (LO)

- THE IMPORTANT **LIPIDS** INVOLVED IN **OXIDATION** ARE THE **UNSATURATED FATTY ACID** MOIETIES e.g. **OLEIC**, **LINOLEIC** & **LINOLENIC**
- THE **RATE OF OXIDATION** OF THESE FATTY ACIDS **INCREASES** WITH THE **DEGREE OF UNSATURATION** (NUMBER OF DOUBLE BONDS)
  - ***Oleic acid*** **(1 Double Bond - MUFA)** **01 times**
  - ***Linoleic acid*** **(2 Double Bonds - PUFA)** **10 times**
  - ***Linolenic acid*** **(3 Double Bonds - PUFA)** **100 times**

LIPID OXIDATION (LO)

- ONCE FORMED, **HYDROPEROXIDES** (ROOH) MAY **BREAK DOWN** THROUGH A **NUMBER OF MECHANISMS**

- A **COMMON** BREAKDOWN **SCHEME** IS CALLED **DISMUTATION**

- IN THIS REACTION A **HYDROPEROXIDE** REACTS WITH ANOTHER **MOLECULE** OR **RADICAL** TO FORM **TWO NEW TYPES OF** COMPOUNDS

LIPID OXIDATION (LO)

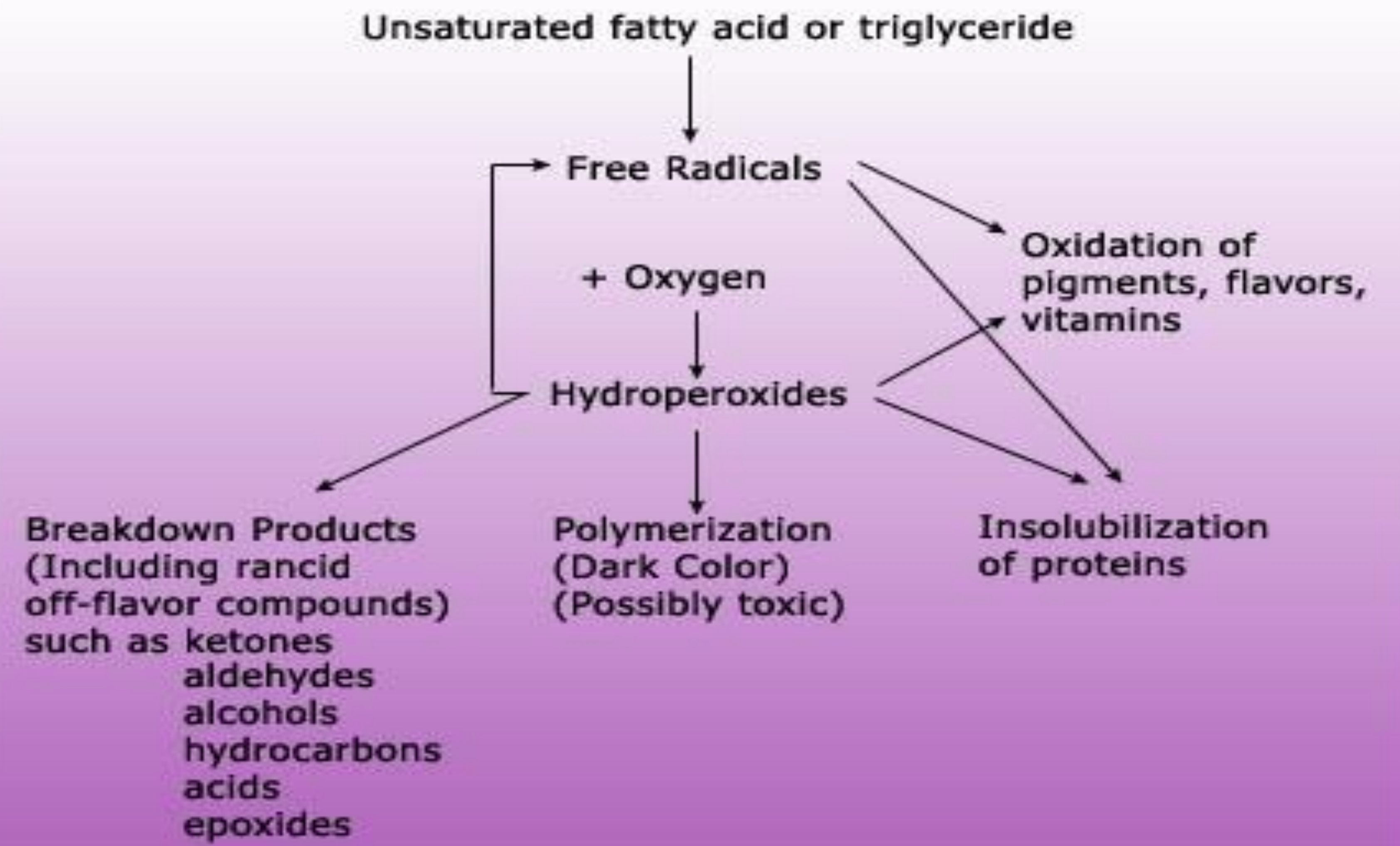
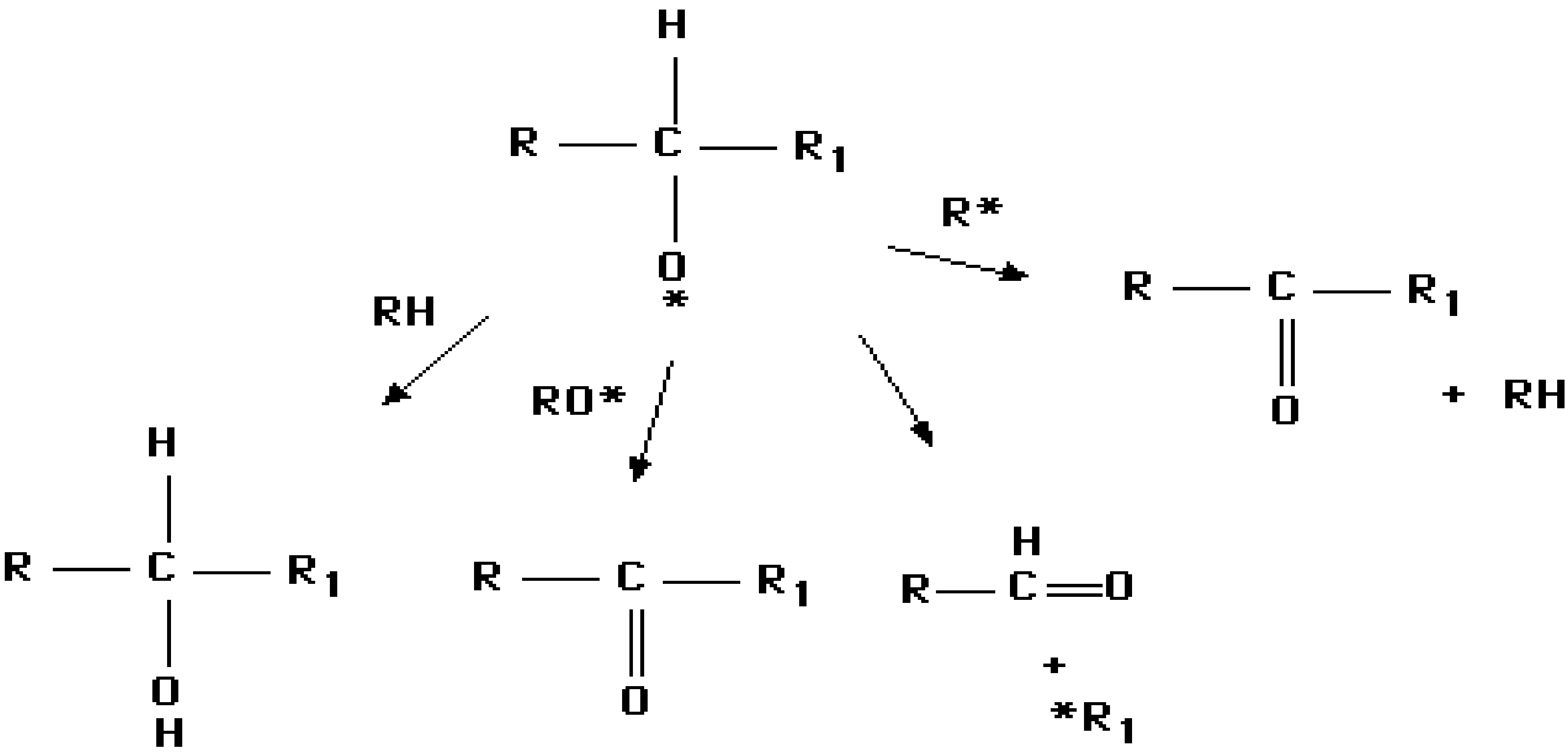


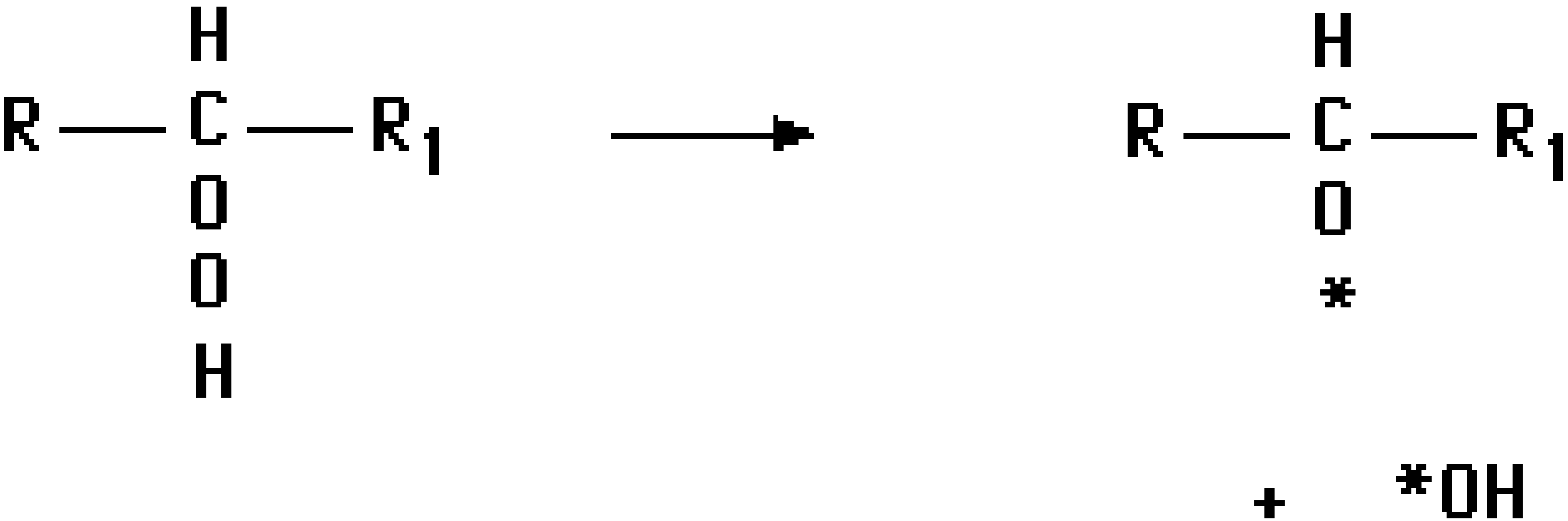
Fig. 1 Lipid Oxidation Mechanism

LIPID OXIDATION (LO)



- THIS REACTION SCHEME IS CAPABLE OF **GENERATING ALDEHYDES**, **KETONES**, **ALCOHOLS** AND **HYDROCARBONS**
- MANY OF THE **VOLATILE** COMPOUNDS FORMED DURING LIPID OXIDATION ORIGINATE THROUGH **SIMILAR DISMUTATIONS**

LIPID OXIDATION (LO)



- **HYDROPEROXIDES** ARE **NOT STABLE** COMPOUNDS AND GIVEN TIME, THEY WILL BREAK DOWN

- A TYPICAL MECHANISM, AS SHOWN BELOW, RESULTS IN THE FORMATION OF **TWO RADICALS** FROM A SINGLE HYDROPEROXIDE MOLECULE

LIPID OXIDATION (LO)

$$Cu^{+} + ROOH \longrightarrow RO^{*} + {}^{-}OH + Cu^{++}$$

$$Cu^{++} + ROOH \longrightarrow ROO^{*} + H^{+} + CU^{+}$$

- BOTH OF THESE **NEW RADICALS** CAN INITIATE FURTHER OXIDATION
- SOME **METALS** CAN SPEED UP THIS REACTION

LIPID OXIDATION (LO)

$$2\ ROOH \longrightarrow RO^* + ROO^* + H_2O$$

- NOTE THAT BOTH **IONS** AND **FREE RADICALS** ARE FORMED
- **COPPER** AS THE CATALYST
- COPPER **DID NOT INITIATE** THE REACTION, BUT ONCE THE **HYDROPEROXIDES** ARE FORMED, IT **SPEED UP** THEIR BREAKDOWN

LIPID OXIDATION (LO)

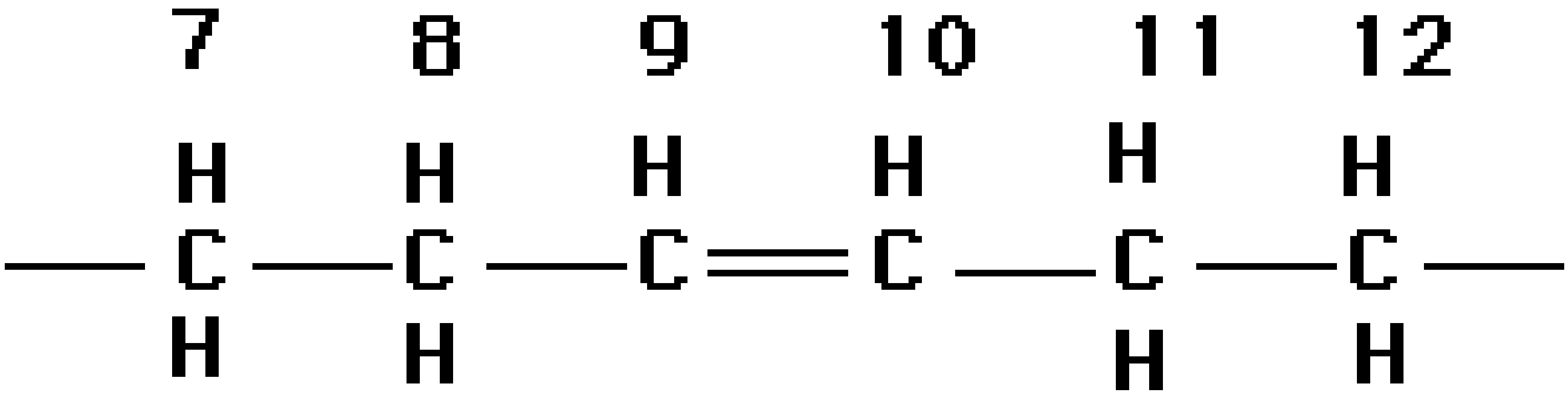
- SINCE THE REACTION **RH + O_2** **FREE RADICALS, IS THERMODYNAMICALLY DIFFICULT**

  (ACTIVATION ENERGY = **35 K. Cal/Mol**)

- THE PRODUCTION OF THE **FIRST FEW RADICALS** NECESSARY TO START THE **PROPAGATION** REACTION NORMALLY MUST OCCUR BY SOME CATALYTIC MEANS SUCH AS

- *HYDROPEROXIDE DECOMPOSITION*
- *LIGHT*
- *HEAT EXPOSURE*
- *METAL CATALYSIS*

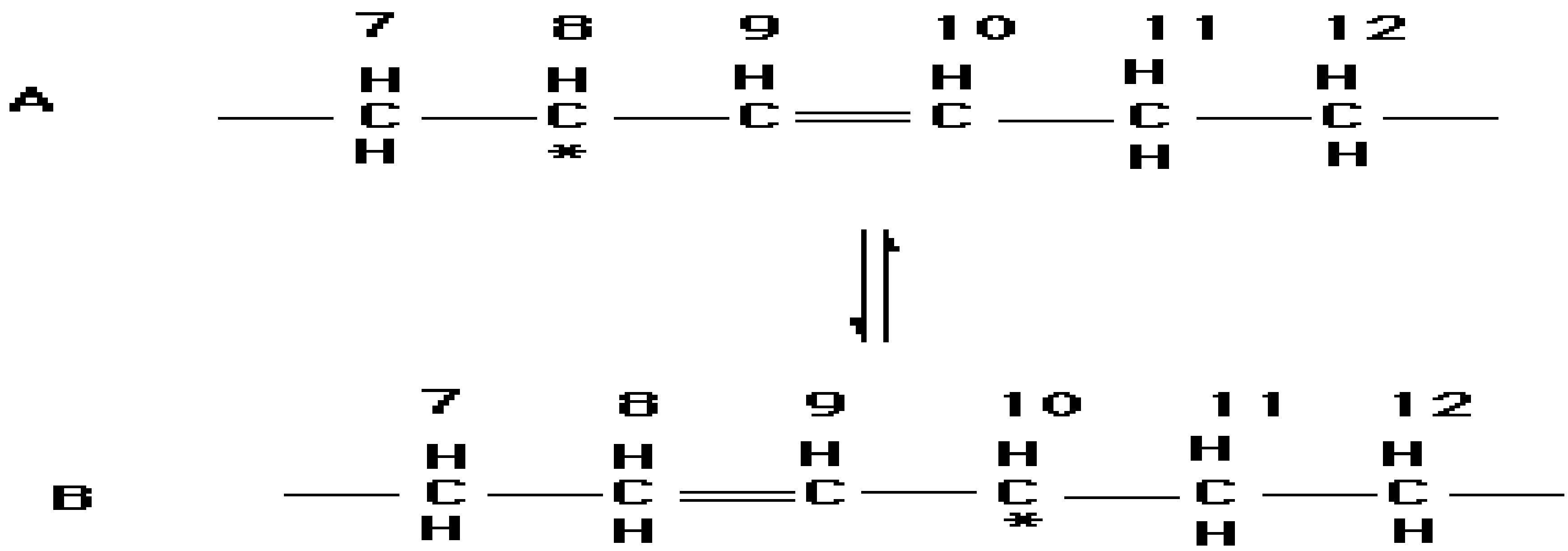
LIPID OXIDATION (LO); A MONOENOIC ACID



OLEIC ACID

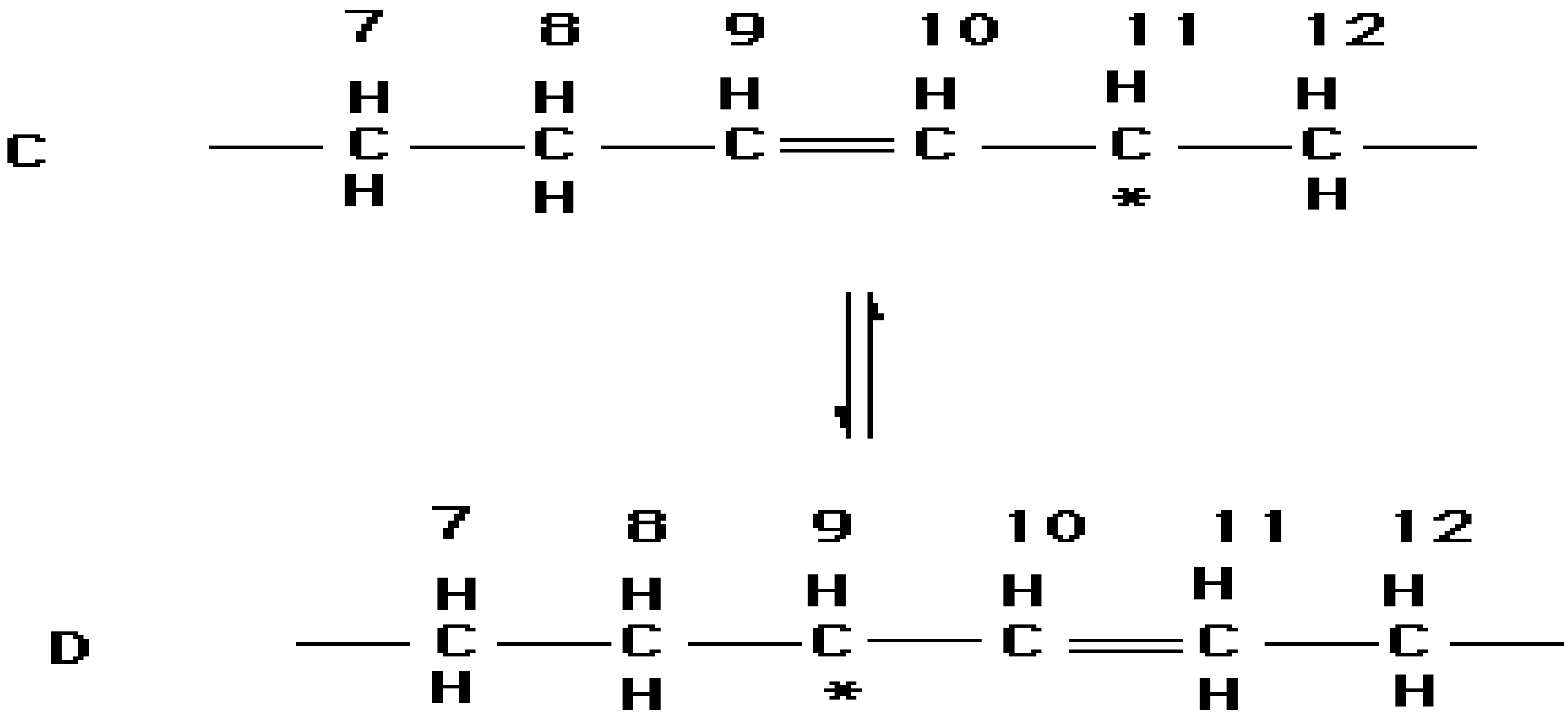
- A **HYDROGEN** COULD BE REMOVED FROM EITHER **C-8** or **C-10**, AS THESE POSITIONS ARE LOCATED **α** TO THE **DOUBLE BOND**

LIPID OXIDATION (LO); A MONOENOIC ACID



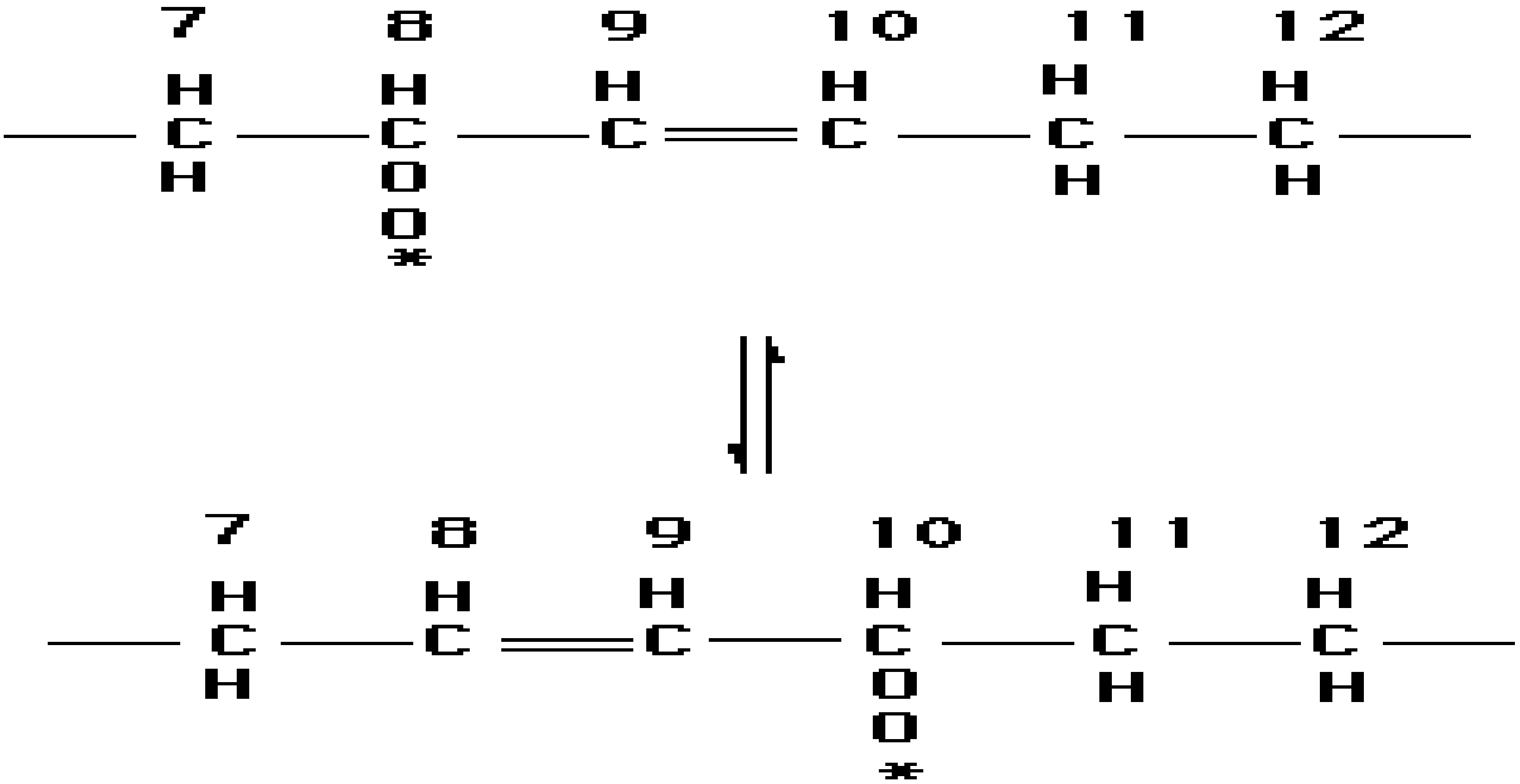
- ABSTRACTION FROM **CARBON 8** RESULTS IN THE **TWO RADICALS A** AND **B** WHICH ARE **POSITIONAL ISOMERS** OF EACH OTHER STABILIZED BY RESONANCE

LIPID OXIDATION (LO); A MONOENOIC ACID



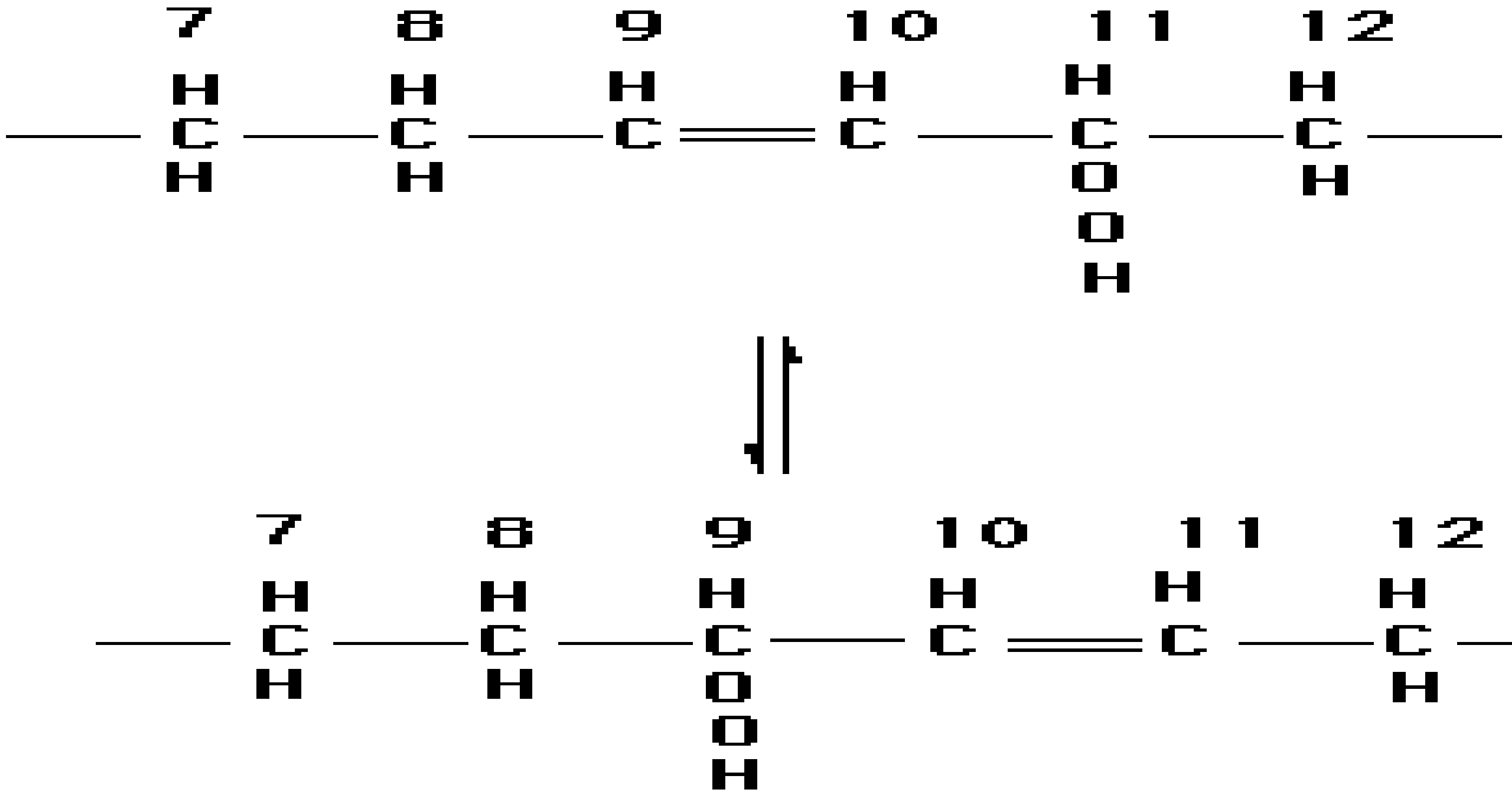
- ABSTRACTION FROM **CARBON 11** CAN OCCUR, RESULTING IN THE **TWO RADICALS C** AND **D**

LIPID OXIDATION (LO); A MONOENOIC ACID



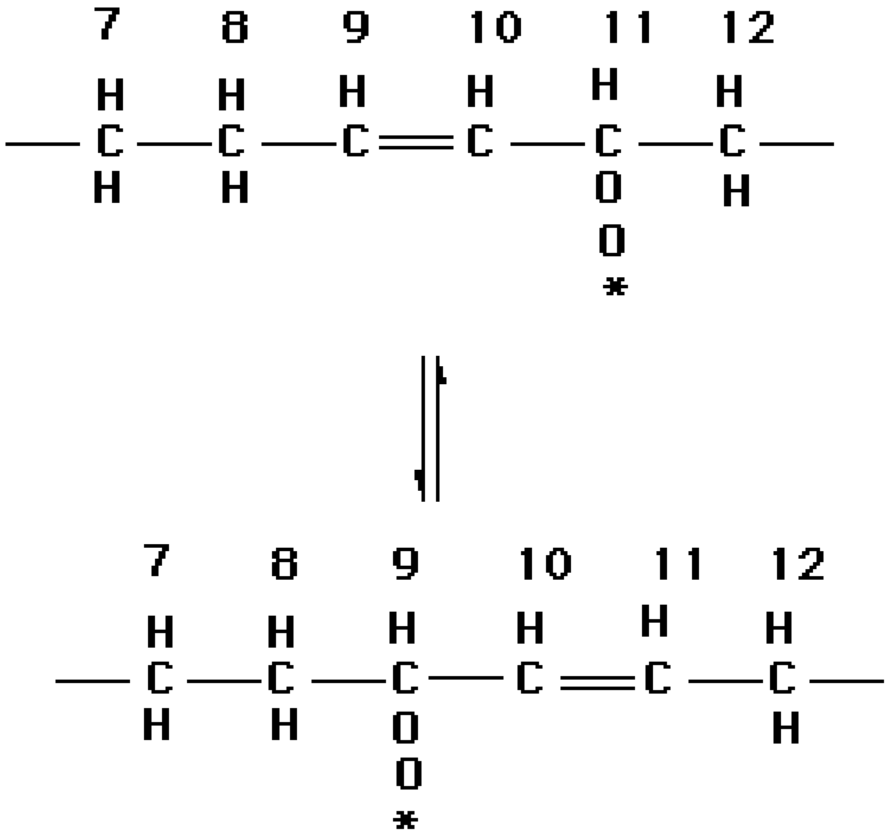
- **OXYGEN** CAN BE **ADDED** TO EACH RADICAL TO FORM **PEROXY RADICALS** AT **C-8**, **C-9**, **C-10** OR **C-11**
- ADDITION TO THE **8** AND **10** POSITIONS YIELD THE **PEROXY RADICALS**

LIPID OXIDATION (LO); A MONOENOIC ACID



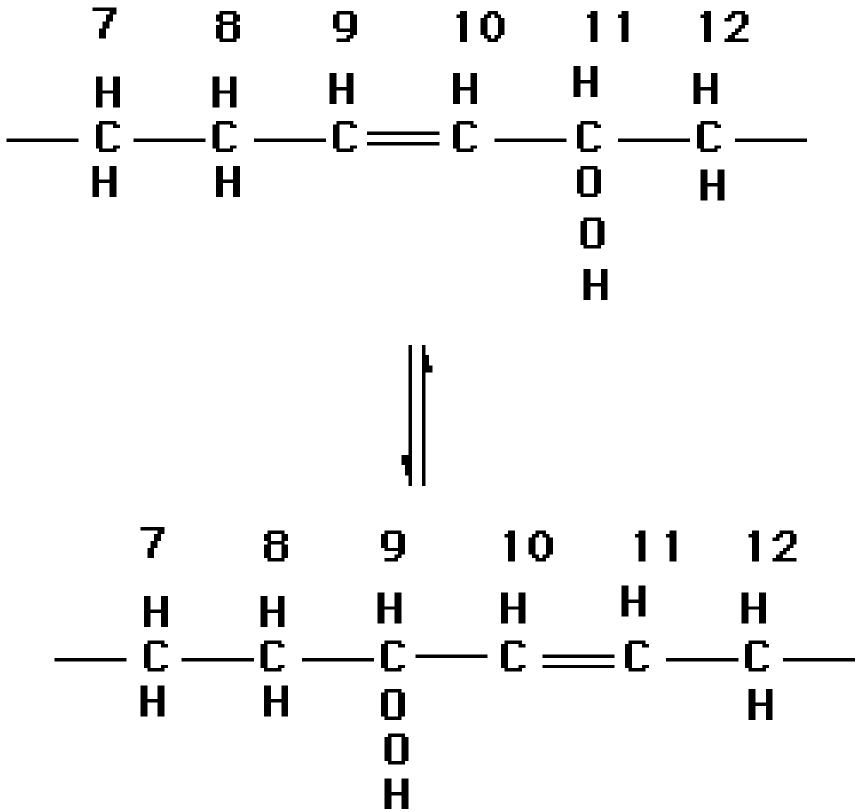
- THESE RADICALS MAY ABSTRACT **H_2** FROM OTHER MOLECULES TO YIELD THE **HYDROPEROXIDES** SHOWN

LIPID OXIDATION OF A MONOENOIC ACID



- THE ADDITION **O_2** AT THE 11 AND 9 POSITIONS RESULTS IN THE **PEROXY** RADICALS

LIPID OXIDATION OF A MONOENOIC ACID



- THE SUBSEQUENT ADDITION OF ABSTRACTED **H_2** MOLECULES RESULTS IN THE **HYDROPEROXIDES** SHOWN

LO MEASUREMENT

PEROXIDE VALUE (PO)

- **PEROXIDES** ARE THE **MAIN INITIAL PRODUCTS** OF **AUTOXIDATION**
- THEY CAN BE **MEASURED** BY **TECHNIQUES** BASED ON THEIR **ABILITY TO LIBERATE I_2** FROM **KI** , OR TO OXIDIZE **FERROUS** TO **FERRIC IONS**
- EXPRESSED AS **MILLIEQUIVALENTS (mEq)** OF **O_2** PER **Kg** OF **FAT**
- ALTHOUGH THE PEROXIDE VALUE IS **APPLICABLE** FOR FOLLOWING PEROXIDE FORMATION AT **THE EARLY STAGES OF OXIDATION**, IT IS, NEVERTHELESS, HIGHLY EMPIRICAL

LO MEASUREMENT

PEROXIDE VALUE (PO)

- THE **ACCURACY** IS QUESTIONABLE, THE RESULTS VARY WITH DETAILS OF THE **PROCEDURE USED**, AND THE TEST IS **EXTREMELY SENSITIVE TO TEMPERATURE CHANGES**
- DURING THE **COURSE** OF OXIDATION, PEROXIDE VALUES **REACH A PEAK** AND **THEN DECLINE**

LO MEASUREMENT

THIOBARBITURIC ACID (TBA)

- **THE MOST WIDELY** USED TEST FOR MEASURING THE EXTENT OF **LO** IN FOODS DUE TO ITS **SIMPLICITY** AND BECAUSE ITS RESULTS ARE HIGHLY **CORRELATED** WITH **SENSORY EVALUATION SCORES**

- THE **BASIC PRINCIPLE** OF THE METHOD IS THE REACTION OF **ONE MOLECULE** OF **MALONALDEHYDE** AND **TWO** MOLECULES OF **TBA** TO FORM A **RED MALONALDEHYDE-TBA COMPLEX**, WHICH CAN BE QUANTITATED **SPECTROPHOTOMETRICALLY** (**530** nm)

- THIS METHOD HAS BEEN **CRITICIZED** AS BEING NONSPECIFIC AND **INSENSITIVE** FOR THE DETECTION OF **LOW LEVELS** OF **MALONALDEHYDE**

LO MEASUREMENT

THIOBARBITURIC ACID (TBA)

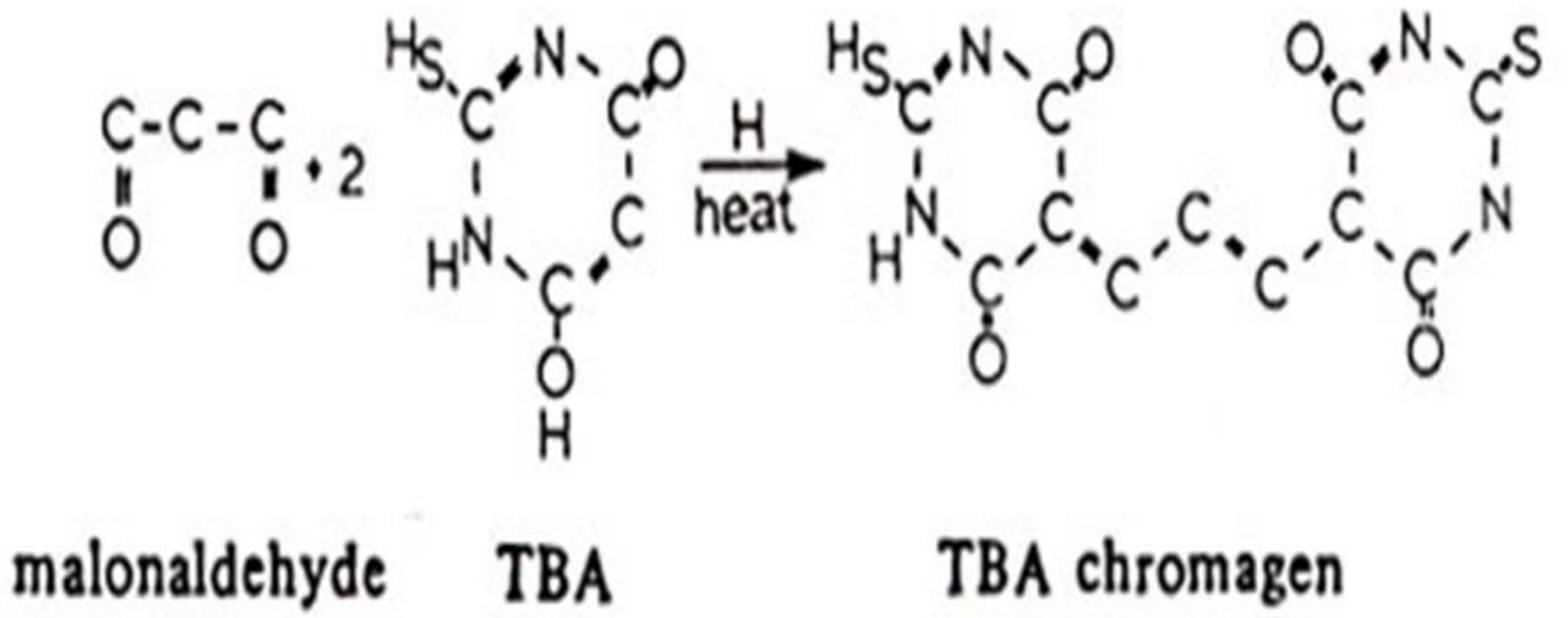
- OTHER **TBA REACTIVE SUBSTANCES (TBARS)** INCLUDING **SUGARS** AND OTHER **ALDEHYDES** COULD INTERFERE WITH THE **MALONALDEHYDE-TBA** REACTION

- ABNORMALLY **LOW VALUES** MAY RESULT IF SOME OF THE MALONALDEHYDE REACTS WITH **PROTEINS** IN AN **OXIDIZING** SYSTEM

- THE **TBA** TEST IS APPLICABLE FOR **COMPARING** SAMPLES OF **A SINGLE** MATERIAL AT **DIFFERENT STATES** OF OXIDATION

LO MEASUREMENT

PROPOSED TBA REACTION



RED MALONALDEHYDE-TBA COMPLEX

LO MEASUREMENT

IODINE VALUE (IV)

- **IODINE VALUE** IS A MEASURE OF THE **UNSATURATED LINKAGES** IN **FAT** AND IS EXPRESSED IN TERMS OF **%** OF **IODINE** ABSORBED

- THE **DECLINE** IN **IODINE VALUE** IS SOMETIMES USED TO MONITOR THE REDUCTION OF **DIENOIC ACIDS** DURING THE COURSE OF THE **AUTOXIDATION**

LO MEASUREMENT

ACTIVE OXYGEN METHOD (AOM)

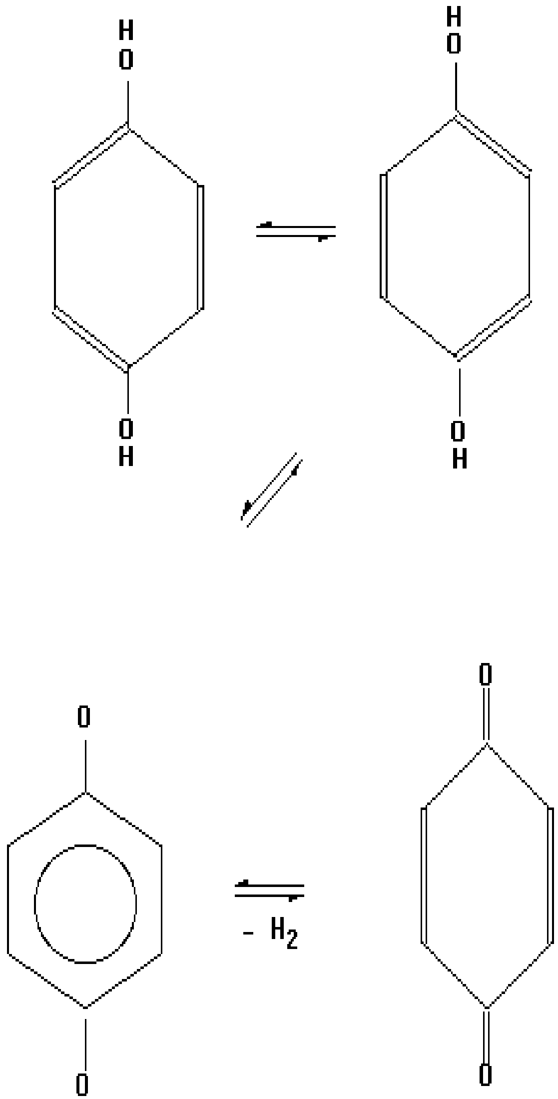
- **IODINE VALUE** OR **PEROXIDE VALUE** IS MEASURED **OVER TIME** AS **OXYGEN** IS **BUBBLED** THROUGH AN **OIL** SAMPLE
- THIS METHOD IS ALSO USED TO **EVALUATE ANTIOXIDANTS**

CONTROLLING OXIDATIVE RANCIDITY

- Antioxidants—substances that are added to slow down oxidation
  - BHA—butylated hydroxyanisole
  - BHT—butylated hydroxytoluane
- Packages that exclude light
- Vacuum packaging
- Adding nitrogen
- Speed up distribution
- Shelf dating
  - length of storage
  - temperature
  - relative humidity
  - light
- Vitamins E and C

LO CONTROL: ANTIOXIDANTS

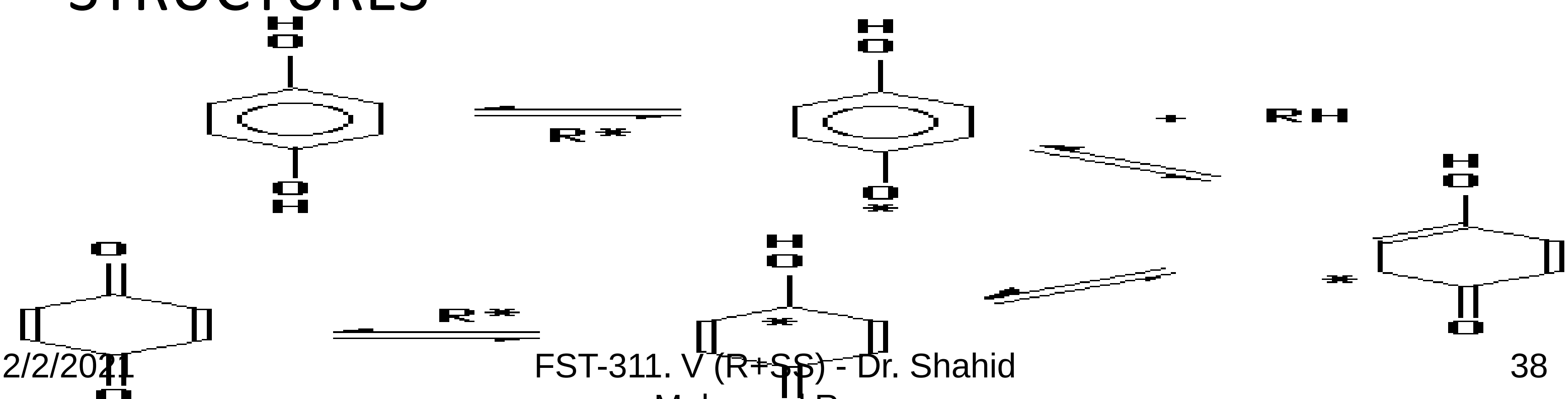
- ANTIOXIDANTS **FUNCTION** BY **INTERFERING** WITH THE **CHAIN REACTION**
- IF THE **NUMBER** OF **FREE RADICALS** CAN BE KEPT **LOW** ENOUGH, **OXIDATION WILL NOT OCCUR**
- THE FOLLOWING IS A MODEL FOR THE TYPE OF COMPOUND THAT CAN FUNCTION EFFECTIVELY AS AN **ANTIOXIDANT**



LO CONTROL: ANTIOXIDANTS

FUNCTION WELL AS AN ANTIOXIDANT A MOLECULE MUST

- **REACT WITH FREE RADICALS MORE RAPIDLY** THAN THE FREE RADICALS REACT WITH **LIPID**
- THE PRODUCTS OF THE REACTION WITH FREE RADICALS MUST NOT BE **PRO-OXIDANT**
- THE MOLECULE MUST BE **LIPID SOLUBLE**
- THE FREE RADICALS FORMED BY CONJUGATED MOLECULES CAN EXIST IN MANY RESONANT STRUCTURES



ALTERNATIVES TO ANTIOXIDANTS

- **ELIMINATION OF OXYGEN**
  - *PACKAGING UNDER **NITROGEN***
  - *PACKAGING IN **VACUUM***
  - *PACKAGING WITH AN **OXYGEN SCAVENGER***
- **ELIMINATION OF THE SENSITIVE SUBSTRATES**
  - *REPLACEMENT OF **POLYUNSATURATED** OILS WITH **LESS UNSATURATED OILS** (**OLIVE OIL** OR **PALM OIL**)*
- **DECREASING THE RATE OF OXIDATION**
  - *STORAGE AT LOW **TEMPERATURES***
  - *STORAGE IN THE **DARK***
  - *USE OF FATS AND OILS THAT CONTAIN LOW LEVELS OF **OXIDATION PROMOTERS** (e.g. **OXIDIZED PRODUCTS** AND **HEAVY METALS**)*
  - *USE OF **INGREDIENTS** THAT ARE **NATURALLY RICH IN ANTIOXIDANTS***

ANTIOXIDANTS

- **BUTYLATED HYDROXY ANISOLE (BHA)**
  - BHA IS A MIXTURE OF **TWO ISOMERS**
  - REFERRED TO AS A **'HINDERED PHENOL'** BECAUSE OF THE **PROXIMITY** OF THE **TERTIARY BUTYL** GROUP TO THE **HYDROXYL** GROUP
  - THIS MAY **HINDER THE EFFECTIVENESS** IN **VEGETABLE OILS**
  - **USES**
    - ***LARD, SHORTENINGS, VEGETABLE OILS, CEREALS, PACKAGE LINERS, POTATO PRODUCTS, DRY SOUPS, CHEWING GUM*** *etc.*
  - USUALLY IN **COMBINATION** WITH OTHER PRIMARY ANTIOXIDANTS

ANTIOXIDANTS

- **PROPYL GALLATE**
  - **THREE HYDROXYL GROUPS** MAKE IT VERY REACTIVE
  - **LOWER SOLUBILITY**
  - TEND TO **CHELATE TRACE MINERALS** SUCH AS **IRON** AND FORM COLORED COMPLEXES
  - **HEAT LABILE**, ESPECIALLY UNDER **ALKALINE** CONDITIONS
  - **USES**
    - ***LARD, SHORTENING, VEGETABLE OILS, CEREALS, PACKAGE LINERS, ANIMAL FEEDS etc.***
  - USED ALONE AND IN COMBINATION WITH **BHA** or **PG** AND **CITRIC ACID**

ANTIOXIDANTS

BUTYLATED HYDROXY TOLUENE (BHT)

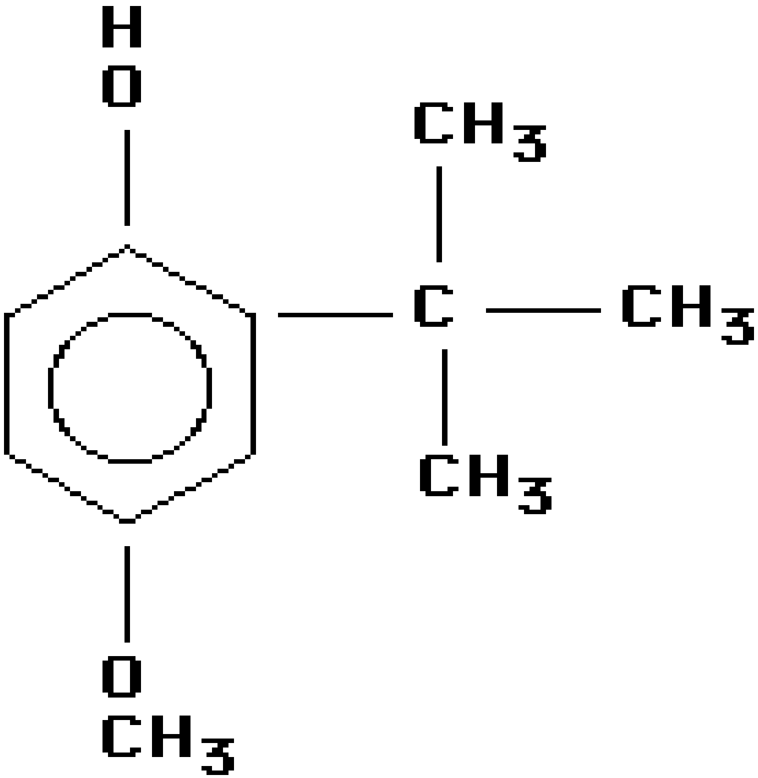
- **BHT** IS ALSO A "**STERICALLY HINDERED PHENOL**"
- SUSCEPTIBLE TO LOSS THROUGH **VOLATILIZATION** IN **HIGH TEMPERATURE** APPLICATIONS
- USES
  - ***LARD, SHORTENING, VEGETABLE OILS, CEREALS, ANIMAL FEEDS etc.***
- USUALLY USED IN COMBINATION WITH **BHA** OR **BHT** AND **CITRIC ACID**

ANTIOXIDANTS

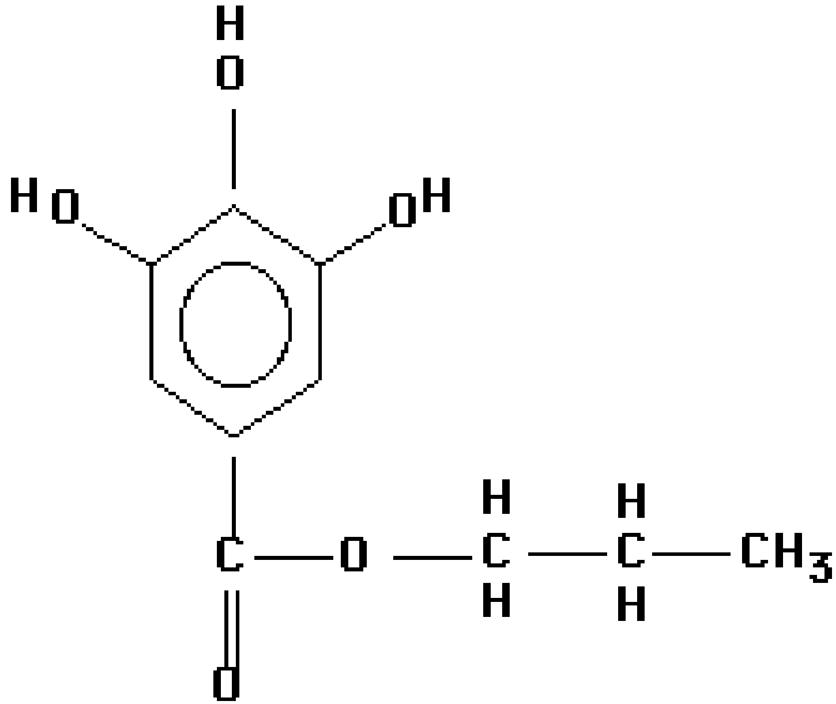
TERTIARY BUTYLATED HYDROQUINONE (TBHQ)

- TBHQ IS AN **EXTREMELY POTENT ANTIOXIDANT**
- HAD BEEN USED EXTENSIVELY IN **NON-FOOD** APPLICATIONS PRIOR TO GAINING APPROVAL IN FOOD
- USES
  - ***LARD, COTTONSEED OIL, POTATO CHIPS, CORN FLAKES etc.***

ANTIOXIDANTS

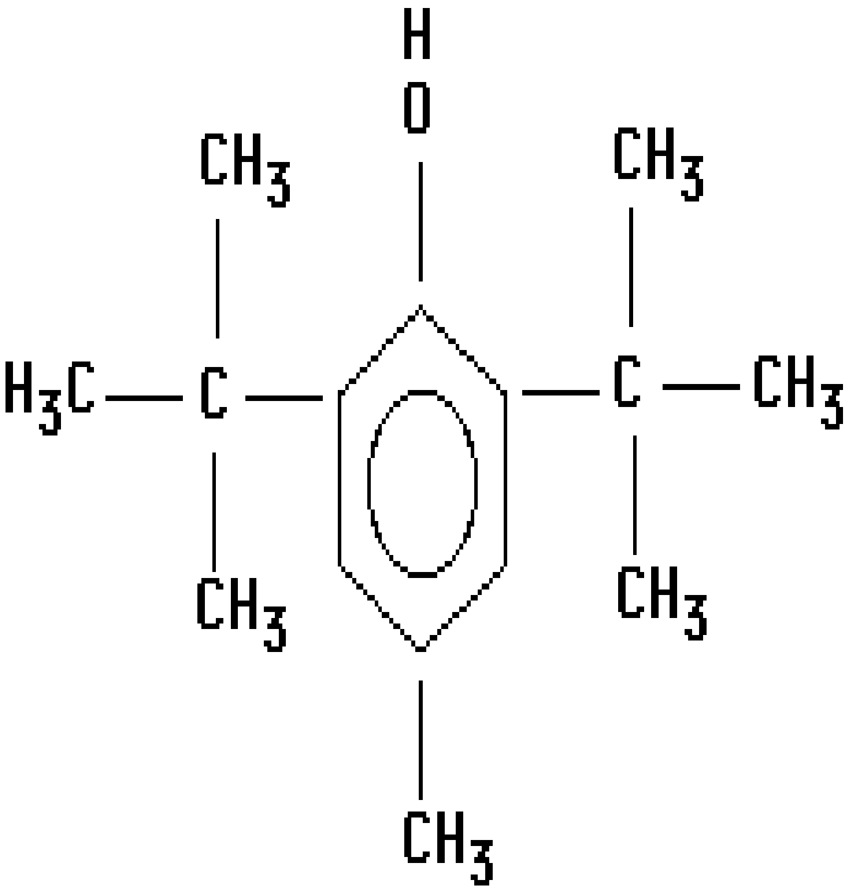


BHA

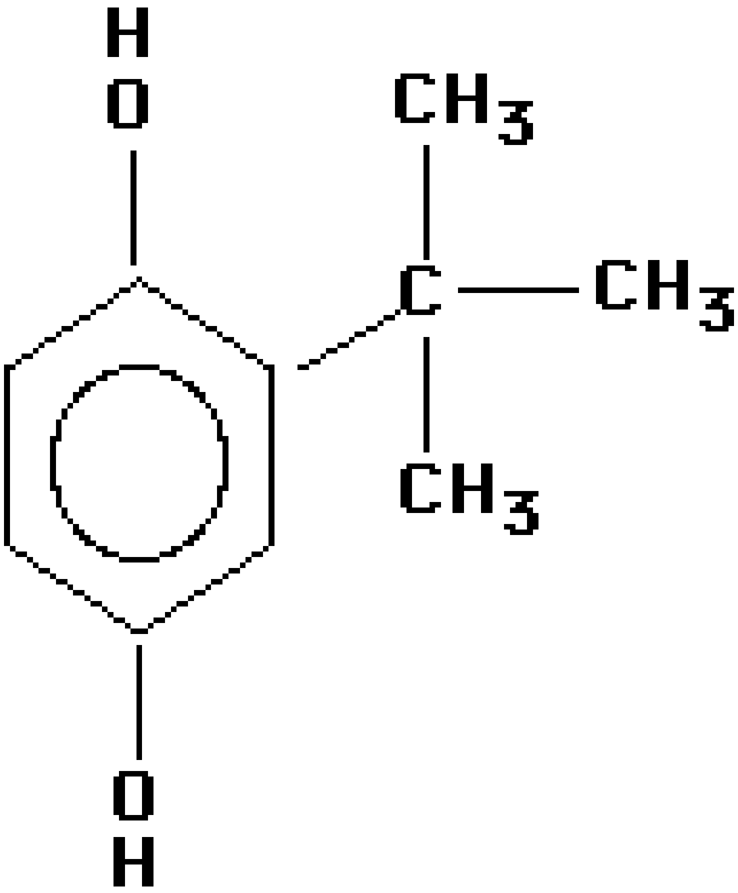


PG

ANTIOXIDANTS



BHT



TBHQ

ANTIOXIDANTS

COMBINATIONS

- ANTIOXIDANTS ARE USUALLY COMBINED TO TAKE ADVANTAGE OF THEIR **DIFFERING PROPERTIES**
- **BHA** MAY BE COMBINED WITH **PG** AND **CITRIC ACID**
- THE **CITRATE CHELATES METALS**
- **PROPYL GALLATE** PROVIDES A HIGH LEVEL OF **INITIAL PROTECTION**
- **BHA** HAS GOOD CARRY THROUGH PROPERTIES

ANTIOXIDANTS

REASONS FOR COMBINATIONS

- **TAKE ADVANTAGE** OF DIFFERENT PROPERTIES
- ALLOW FOR **BETTER CONTROL** AND **ACCURACY**
- MAY PROVIDE **SYNERGISTIC** EFFECTS
- COMBINATIONS MAY PROVIDE MORE **COMPLETE DISTRIBUTION** IN SOME FOODS
- MORE **CONVENIENT** TO HANDLE

ANTIOXIDANTS

USES OF ANTIOXIDANTS

- **FATS** AND **OILS** (LESS EFFECTIVE IN HIGHER POLYUNSATURATES)
- **FOODS** MADE WITH **FATS** (**POTATO CHIPS, NUTS, CANDIES, PRE-MIXES, FROZEN PIES**)
- FOODS WITH **FATTY CONSTITUENTS** (**PEPPERS, OTHER SPICES, CEREALS, DEHYDRATED VEGETABLES, CITRUS OILS, CHEWING GUM**)

NATURAL ANTIOXIDANTS; PROPERTIES

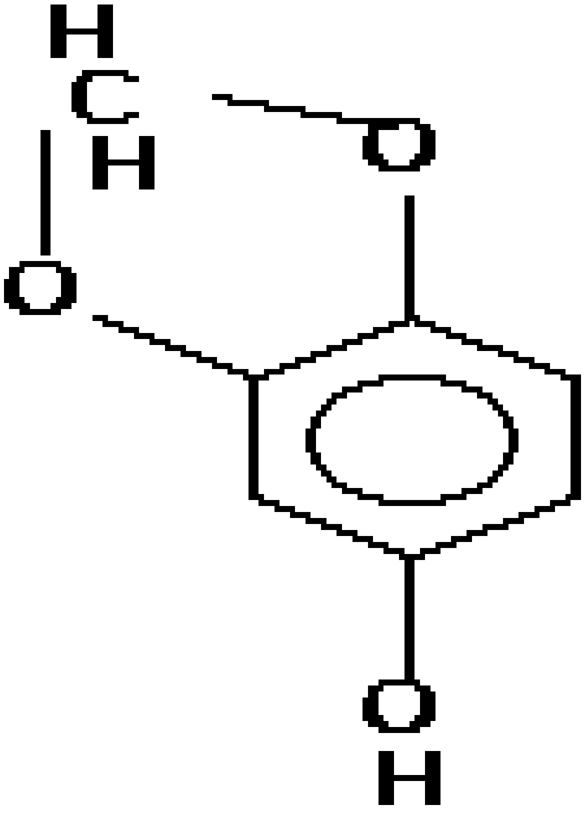
- SHOULD NOT CAUSE **OFF FLAVORS** OR **COLORS**
- MUST BE **LIPID SOLUBLE**
- MUST BE **NON TOXIC**
- SHOULD HAVE **CARRY THROUGH PROPERTIES**
- MUST BE **COST-EFFECTIVE**

NATURAL ANTIOXIDANTS

SESAME

- CONTAINS **SESAMOL**
- MORE **EFFECTIVE** IN **LARD** THAN **BHA** OR

  BHT

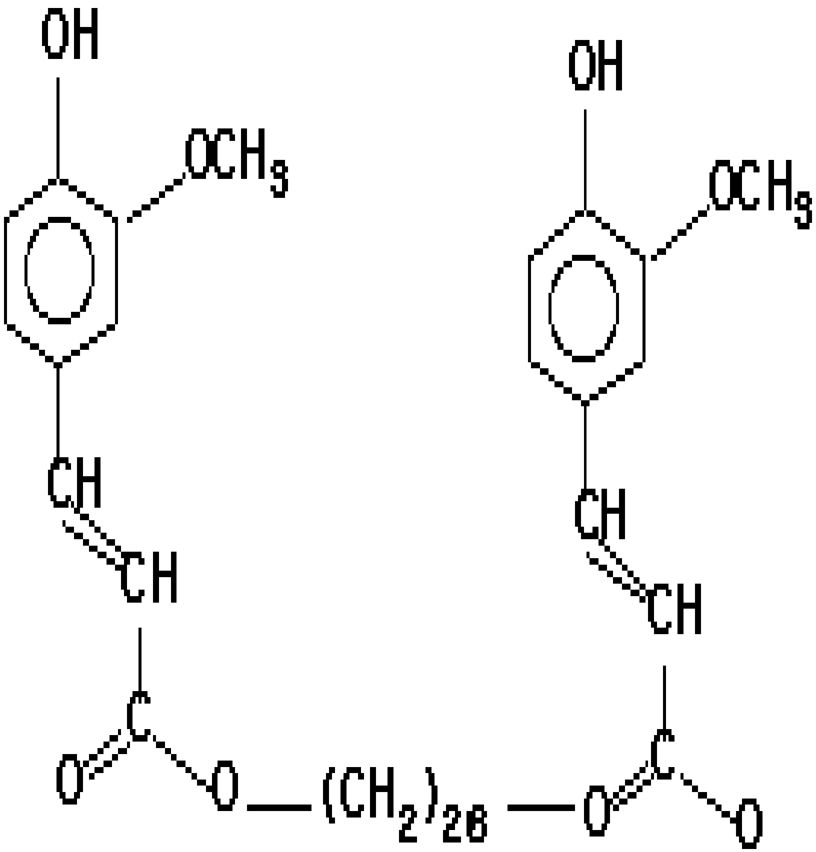


SESAMOL

NATURAL ANTIOXIDANTS

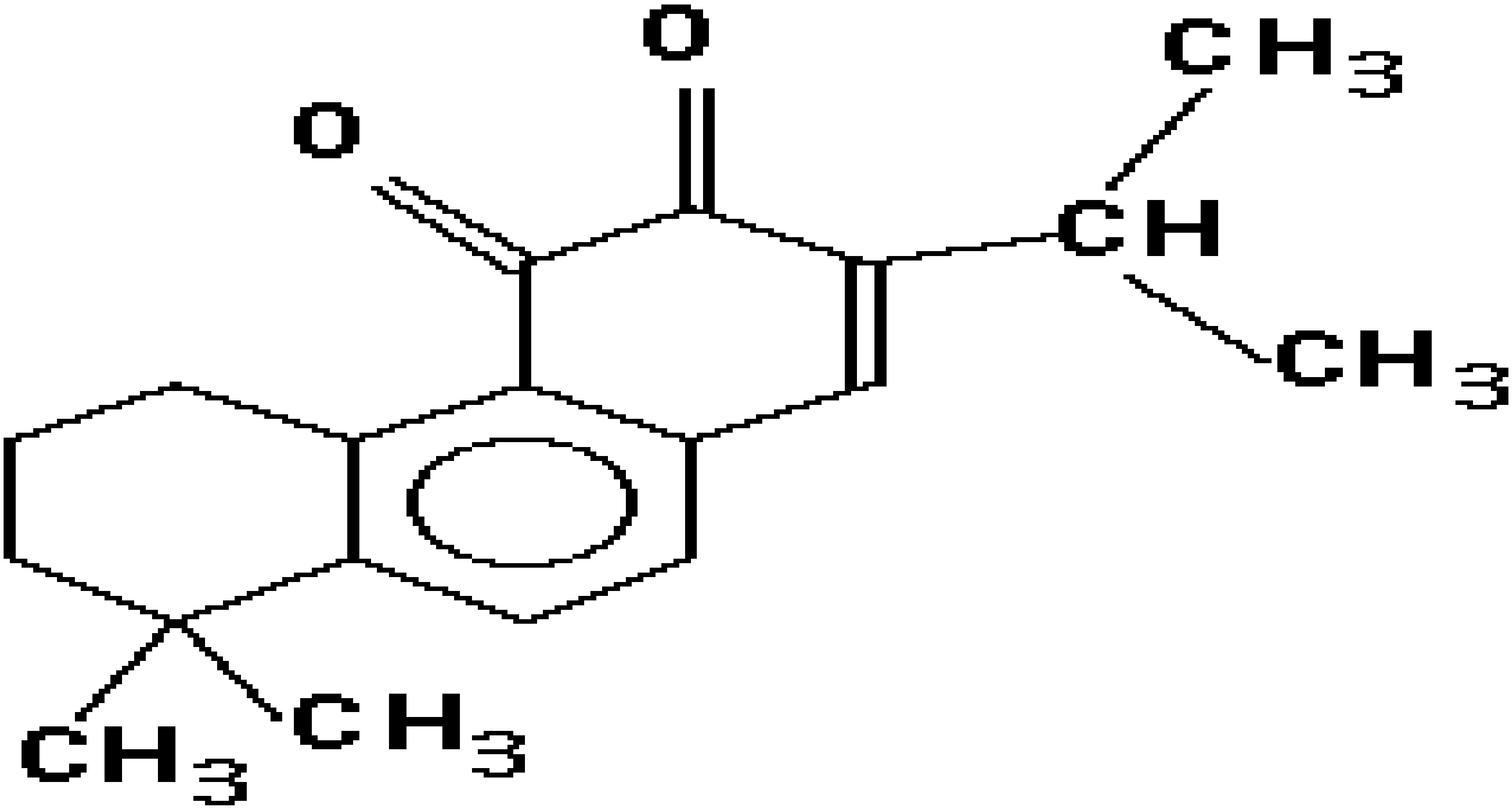
OATS

- HAVE BEEN RECOGNIZED TO HAVE **ANTIOXIDANT PROPERTIES**
- OVER **25 PHENOLIC** COMPOUNDS HAVE BEEN IDENTIFIED IN OATS
- MANY DERIVED FROM **CAFFEIC** AND **FERULIC ACID**



Hexacosane-1,26-Diol Diferulate

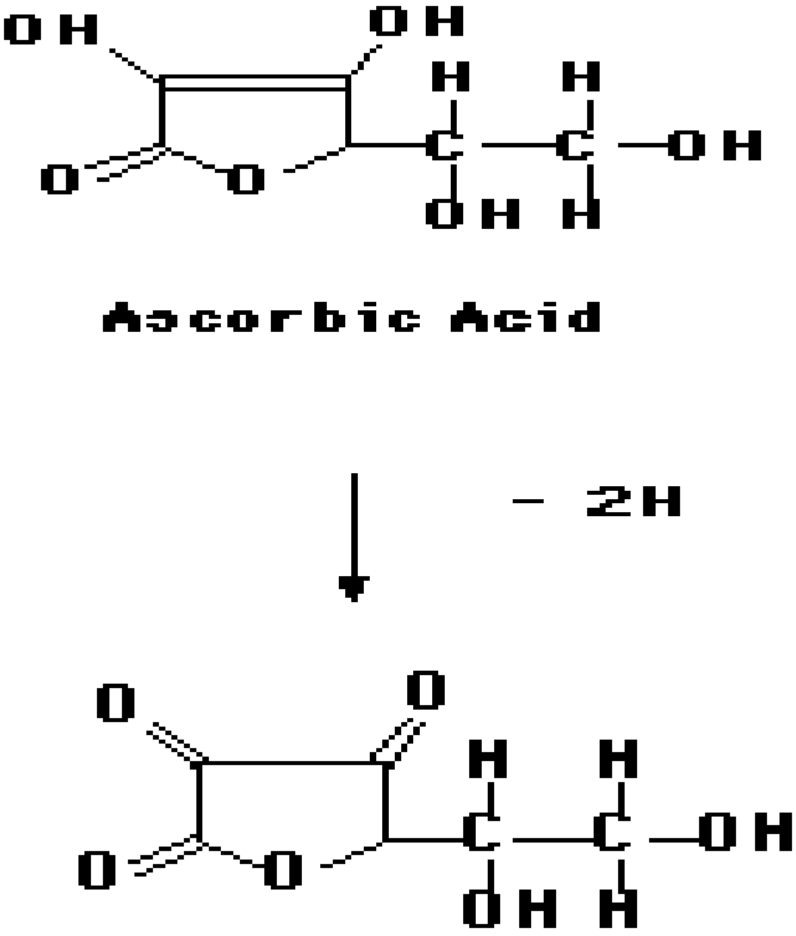
NATURAL ANTIOXIDANTS



ROSMARIQUINONE

NATURAL ANTIOXIDANTS

Ascorbic Acid



Dehydroascorbic Acid

FRYING

INDUSTERIAL APPLICATION

OF

LIPIDS

IN

MODERN FOODS

FRYING

- FRYING IS **COOKING FOOD** IN **FAT** OVER **MODERATE** TO **HIGH HEAT**
- FRYING IS THE COOKING OF FOOD IN **OIL** OR ANOTHER **FAT**
- VARIETY OF LIPIDS
  - ***LARD***
  - ***RAPESEED OIL***
  - ***OLIVE OIL***
  - ***CANOLA***
  - ***CORN***
  - ***GRAPESEED***
  - ***PEANUT***
  - ***SAFFLOWER***
  - ***SUNFLOWER***

FRYING

FRYING TYPES

- **STIR FRYING**
- **PAN FRYING**
- **SHALLOW FRYING**
- **DEEP FRYING**

CHARACTERISTICS OF FRYING

MASS TRANSFER

- **WATER** IN A FRYING FOOD MIGRATES FROM THE **CENTER** TO THE **SURFACE**
- AS WATER IS **REMOVED** AT THE **SURFACE** DUE TO HEATING, WATER IS '**PUMPED**' TO THE SURFACE
- THE **RATE** OF **WATER LOSS** AND ITS **EASE** OF **MIGRATION** THROUGH THE PRODUCT ARE **IMPORTAN**T TO THE **FINAL CHARACTERISTICS** OF THE FOOD

HEAT TRANSFER

- **WATER EVAPORATION** FROM THE SURFACE OF A FRYING FOOD ALSO REMOVES HEAT FROM THE SURFACE AND INHIBITS **CHARRING** OR **BURNING** AT THE SURFACE
- THE **HEAT OF VAPORIZATION** OF WATER TO STEAM **REMOVES** MUCH OF THE **HEAT** AT THE **FOOD/OIL SURFACE**

CHARACTERISTICS OF FRYING

HEAT REMOVAL

- AS LONG AS **WATER** IS BEING REMOVED AT A **SUFFICIENT RATE**, THE **SURFACE** OF THE FOOD WILL NOT **CHAR**
- **SUBSURFACE WATER** IN THE FOOD WILL ALSO **CONDUCT HEAT AWAY** FROM THE **SURFACE**

INTERIOR COOKING

- **TRANSFER** OF **HEAT** TO THE **INTERIOR** OF THE PRODUCT BY **WATER** WILL RESULT IN **COOKING** OF THE **INTERIOR** OF THE FOOD
- NEED **ENOUGH HEAT** TO '**COOK**' THE PRODUCT, BUT NOT ENOUGH TO CAUSE **DAMAGE**
- e.g. **FRENCH FRY**

CHARACTERISTICS OF FRYING

OIL-FOOD INTERACTIONS

- **IDEALLY** THE FOOD **PRODUCTS** SHOULD HAVE **SIMILAR DIMENSIONS** AND THUS, SIMILAR **SURFACE TO VOLUME** RATIOS
- **ONCE AN EQUILIBRIUM** IS ESTABLISHED ALL **PROCESSES** SHOULD BE THE **SAME** UNLESS THERE ARE CHANGES IN **EQUIPMENT FUNCTION** OR IN **OIL COMPOSITION**

OIL

- THE **PROPERTIES** OF **OIL CHANGE** WITH **FRYING**
- **NEW OIL** HAS A **HIGH HEAT CAPACITY** THAT DIMINISHES WITH USE
- **VISCOSITY** MAY CHANGE DRAMATICALLY WITH USE

FRYING - STAGES OF OIL

BREAK IN OIL

- WHITE PRODUCT
- RAW
- UNGELATINATIZED STARCH AT CENTER OF FRY
- NO COOKED ODORS
- NO CRISPING OF THE SURFACE
- LITTLE OIL PICKUP BY THE FOOD

FRESH OIL

- SLIGHT BROWNING AT EDGES OF FRY
- PARTIALLY COOKED (GELATINIZATION) CENTERS
- CRISPING OF THE SURFACE
- SLIGHTLY MORE OIL ABSORPTION

FRYING - STAGES OF OIL

OPTIMUM OIL

- GOLDEN BROWN COLOR
- CRISP, RIGID SURFACE
- DELICIOUS POTATO AND OIL ODORS
- FULLY COOKED CENTERS
- OPTIMAL OIL ABSORPTION

DEGRADING OIL

- DARKENED and/or SPOTTY SURFACES
- EXCESS OIL PICKUP
- PRODUCT MOVING TOWARDS LIMPNESS
- CASE HARDENED SURFACES

FRYING - STAGES OF OIL

RUNAWAY OIL

- DARK, CASE HARDENED SURFACES
- EXCESSIVELY OILY PRODUCT
- SURFACES COLLAPSING INWARD
- CENTERS NOT FULLY COOKED
- OFF-ODOR AND FLAVORS (BURNED)

FRYING - QUALITY OF OIL

INDICATORS OF FRYING OIL QUALITY

- TOTAL POLAR COMPOUNDS
- CONJUGATED DIENES
- FFA
- DI-ELECTRIC CONSTANT
- pH
- VISCOSITY
- COLOR
- ODOR
- TASTE

Antioxidants

Stability of
Bakery Products
(AOM –
Days of stability)

Treatment		Pastry		Cracker
Control		2		3
.005 TBHQ		2		7
.001 TBHQ		3		10
.020 TBHQ		4		5
.005 BHA		8		12
.010 BHA		21		22
.020 BHA		27		33
.005 BHT		5		10
.010 BHT		10		14
.020 BHT		19		21
.005 PG		2		3
.010 PG		5		6
.020 PG		3		11

Hydrogenation

- Treatment of an oil with hydrogen and a suitable catalyst to decrease the number of double bonds and increase the degree of saturation

Hydrogenation

- Rate is determined by:
  - Nature of substrate
  - Type and concentration of catalyst
  - Pressure (Concentration of hydrogen)
  - Temperature
  - Agitation

Hydrogenation

- Stages in Hydrogenation
  - Transfer and/or diffusion
  - Adsorption
  - Hydrogenation/Isomerization
  - Desorption
  - Transfer

Hydrogenation

- Transfer and adsorption are critical steps in controlling the degree of isomerization and selectivity of the reaction.
- Transfer of reactants and products to and from the bulk liquid oil phase and the surface of the catalyst.

Hydrogenation

- Diffusion
  - Diffusion of reactants into pores on the catalyst surface. Diffusion of products out of the catalyst surface pores.

Hydrogenation

- Selectivity
  - Define selectivity as the ratio of the rate of hydrogenation of linoleic acid to that of oleic acid.
  - Commonly observed selectivities range for 4 to 50.
  - This would mean linoleic acid is hydrogenated 4 to 50 times faster than oleic acid
  - Desire highly selective catalysts. Why?

Characteristics of some food lipids

Lipid	Iodine Value	% Saturated	% Oleic	% Linoleic
Olio Oil	46.8	47.6	50.1	2.3
Butter Oil	39.5	57.8	38.3	3.9
Chicken Fat	86.5	23.4	52.9	23.7
Cocoa Butter	36.6	60.1	37.0	2.0
Corn Oil	127.0	8.8	35.5	55.7
Cotton Seed	106.0	26.7	25.7	47.5
Lard	66.5	37.7	49.4	12.3
Olive Oil	89.7	2.9	89.5	7.6
Palm Oil	53.6	47.3	42.9	9.8
Peanut oil	93.0	17.7	65.5	25.8
Safflower Oil	144.0	5.7	21.7	72.6
Soybean Oil	136.0	14.0	22.9	55.2

Hydrogenation

- Rate of oxidation of fatty acids, their esters and triglycerides.

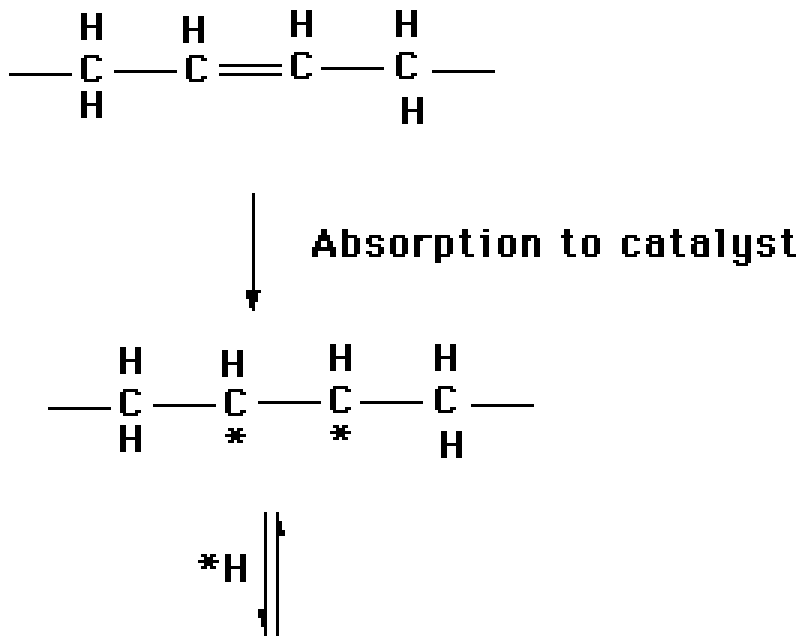
	Acid	Methyl Ester	Triglyceride
Oleic	1	1	1
Linoleic	27	30	27
Linolenic	77	87	97
Arachidonic			114

Hydrogenation

Effects of Hydrogenation

Before	**After**
Unsaturated	Saturated
Liquid	Solid
Cis	Cis/Trans

Hydrogenation



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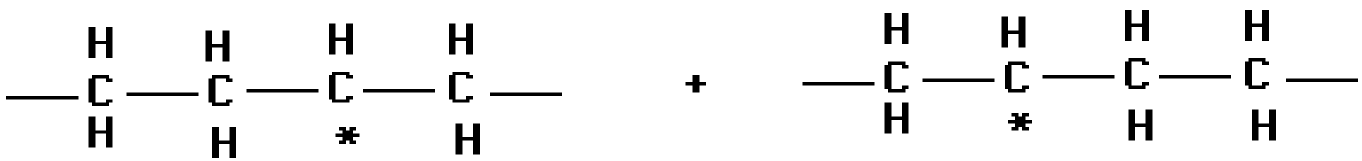

Hydrogenation

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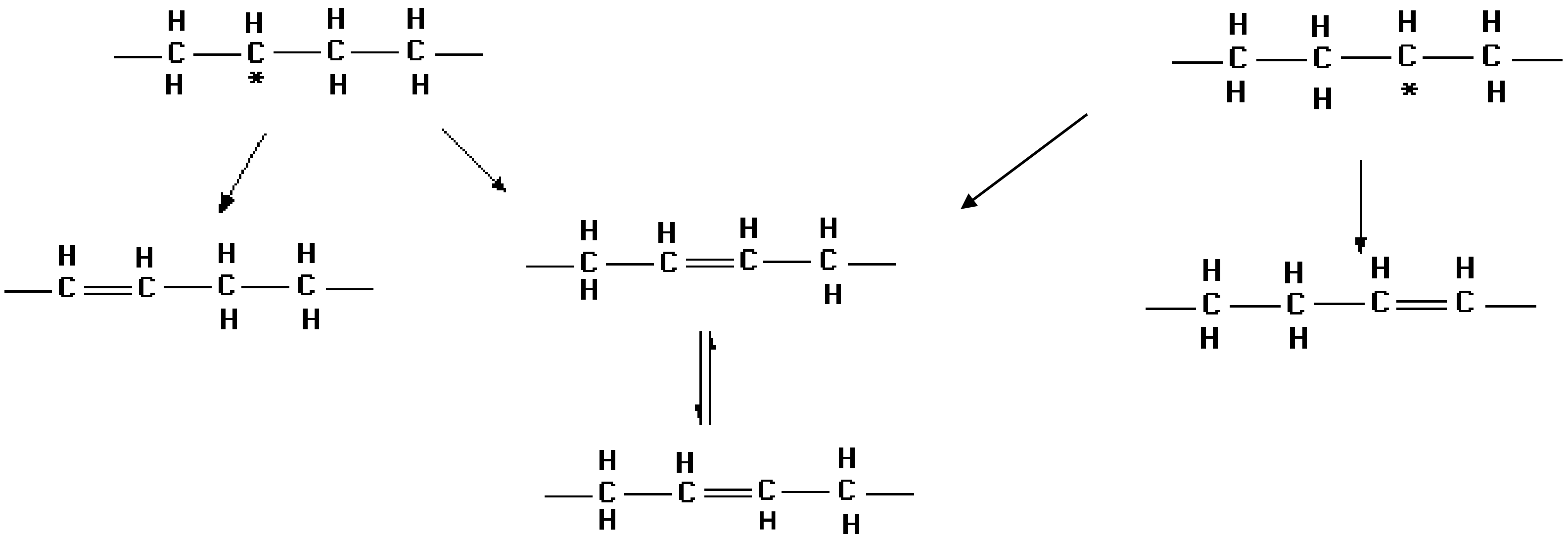

Obtain both cis and trans isomers

Hydrogenation

The effects of processing conditions on hydrogenation

Parameter	Selectivity	Formation of Trans bonds	Reaction Rate
Correlation Direction			
Temperature	Positive	Positive	Positive
Pressure	Negative	Negative	Positive
Concentration	Positive	Positive	Positive
Agitation	Negative	Negative	Positive

Hydrogenation

The effects of hydrogenation include:

Isomerization	Temperature
Δ 9 cis	13.4 °C
Δ 9 trans	44 C
Δ 12 cis	9.8 °C
Δ 12 Trans	40 ° C

Hydrogenation

- Method

  Oil is heated with catalyst (Ni), heated to the desired temperature (140-225°C), then exposed to hydrogen at pressures of up to 60 psig and agitated.
- An example of heterogeneous catalysis.

Hydrogenation - Conditions

- Starting oil must be:
  - Refined
  - Bleached
  - Low in soap
  - Dry
- The catalysts must be:
  - Dry
  - Free of CO_2 and NH_4

Hydrogenation

- Heterogeneous Catalysts
- Most commonly utilized
  - Catalysts and reactants exists in different physical states
  - Hydrogenation reaction takes place on surface of catalyst
  - Nickel containing catalysts are most frequently utilized

Hydrogenation

Nickel Catalysts

- Typical Ni catalyst is usually reduced Ni dispersed in the absence of air into hardened fat to stabilize it. In such systems, the support plays an essential role in determining the specific reactivity of the catalyst.

- Advantages of Nickel
  - Availability
  - Low Cost
  - Inert nature of metal to the oil

Hydrogenation

- Hydrogenation Limitations
  - Selectivity is never absolute
  - Little preference for C18:3 over C18:2
  - Important amounts of trans acids are formed
  - Selectivity and isomerization are linked

Hydrogenation

Isomerization

- An equilibrium will be established between positional and geometric isomers in the mixture.
- Double bonds that are reformed tend to have a trans/cis ration of 2:1. All trans would be expected if there were no steric considerations.

Hydrogenation

Isomerization

- Purposes
  - Convert liquid fats to plastic fats
  - Improve oxidative stability
  - Covert soft fats to firmer fats