4. AUTOXIDATION AND OTHER LIPID REACTIONS

A) Technologically significant reactions (oleochemistry)

1. esterification

   enzymatic (lipases)
   nonenzymatic (acid and base catalysis)

1.1 esterifications
   20-100 °C, H₂SO₄, HCl
   \[ R\text{-OH} + R^1\text{-COOH} \rightarrow R^1\text{-COOR} + H₂O \]
   glycols, alditols + FA \( \rightarrow \) emulsifiers
   glycerol + FA (hydroxyl acid) \( \rightarrow \) emulsifiers

1.2 interesterification

   acidolysis
   \[ R^1\text{-COOR} + R^2\text{-COOH} \rightarrow R^2\text{-COOR} + R^1\text{-COOH} \]
   without catalyst, 250-300 °C; with catalyst H₂SO₄, 150-170 °C
   TAG + abietic acid. \( \rightarrow \) varnish
   TAG + phthalic acid \( \rightarrow \) glyptals
   (drying oil ~ natural resins
   exchange lower/higher FA \( \rightarrow \) coconut oil, palm kernel fat

   alcoholysis
   \[ R^1\text{-COOR} + R^2\text{-OH} \rightarrow R^1\text{-COOR}^2 + R\text{-OH} \]
   NaOH, NaOR 20 °C and more, H₂SO₄ ~ 100 °C, with catalyst at 250 °C
   methanolysis \( \rightarrow \) Me-esters, biofuels
   butanolysis \( \rightarrow \) Bu-esters (plasts softenings)
   glycerolysis \( \rightarrow \) parcial esters (emulsifiers)
   transesterification
   \[ R^1\text{-COOR} + R^2\text{-COOR}^3 \rightarrow R^1\text{-COOR}^3 + R^2\text{-COOR} \]
   without catalyst ~ 250 °C, acidic, basic catalyst < 100 °C
   cacao butter, randomisation (melting point higher for about 20 °C)
   oil + tallow \( \rightarrow \) digestability, consistence

2. molecule splitting

   \[ H₂O \]

   \[ R^1\text{-COOR} \rightarrow R^1\text{-COOH} + R\text{-OH} \]

   saponification 1-2 MPa
   hydroxides, soaps as products
3. Hydrogenation

-CH=CH- $\rightarrow$ -CH$_2$-CH$_2$-

H$_2$, 150-200 °C, Ni-catalyst; 0,1-0,2 MPa

Hardened fats (hardening, hydrogenation)

Composition of fatty acids (book 1, tab.3.43)

Stability against oxidation, consistency, absence of trans-acids

Side-reactions

- cis/trans isomerisation (30-45 % trans-isomers)
- positional isomerisation (unusual isomers)

Hydrogenation smell: $\alpha$-linolenic $\rightarrow$ (Z,E)-oktadeca-9,15-dienoic $\rightarrow$ (E)-non-6-enal

Other products (fatty alcohols, ethers)

- FA $\rightarrow$ R-OH ($\sim$ 20 MPa)
- esters $\rightarrow$ ethers type R-O-R$^j$ (nonresorbate fats)

B. Rancidity of oils and fats

- Hydrolytic rancidity
- Scented rancidity
- Reversion
- Oxidation

Hydrolytic rancidity

- Enzymatic reaction: lipases (butter, coconut oil, palm oil)
- Chemical reaction: frying

TAG $\rightarrow$ FA + partial esters

- Butter, milk, coconut oil, palm oil undesirable
- Chocolate partly desirable
- Cheese desirable

Threshold value (mg/kg) free fatty acids, smell, taste (bitter)
scented rancidity
- enzymatic reaction: mikroorganisms and their enzymes
- FA with short and medium carbon chain

- milk fat, coconut oil, palm oil  undesirable
- mould cheese  desirable

reversion
chemical reaction (autooxidation)
wornish, fish and bean smell in oils containing C_{18:3} acids (soybean oil)

oxidative rancidity
- consequences
  negative
  lowering of sensory quality
  lowering of nutritive value, reaction of oxidised lipids with proteins
  lowering of hygiene-toxicological quality, toxic products
  aging, illness (*in vivo*)
  positive
  formation of aromatic compounds

- nonenzymatic reaction
  air oxygen (^{3}\text{O}_{2})
  reactive forms of oxygen (singlet oxygen, radicals, H_{2}O_{2})
  singlet oxygen ^{1}\text{O}_{2}
    formation: photosensitised reactions ^{3}\text{O}_{2}
    pigments (riboflavin, chlorophyll, hem)
    free radicals
      •O_{2}^{-} (superoxide radical)
      •OH^{-} (hydroxyl radical)

- enzymatic reactions
  lipoxygenases (lipoxidases)
nonenzymatic reactions

oxidation by triplet oxygen, autoxidation

general mechanism of hydrocarbon chain autoxidation
(radical reaction)

1. induction stage

\[
R-H \rightarrow R\cdot + \cdot H
\]

hydrocarbon radical

 iniciators, homolytic decomposition

2. propagation stage

\[
R\cdot + O_2 \rightarrow R-O-O\cdot
\]

hydroperoxyl radical

\[
R-O-O\cdot + R-H \rightarrow R-O-O-H + R\cdot
\]

hydroperoxide

up to thousands of segments (influence temperature \(pO_2\).)

hydroperoxide = primary oxidation product

hydroperoxides decomposition

3. terminal stage

mutual radical reactions, polymers of different type

\[
R\cdot + R\cdot \rightarrow R-R
\]

bound C-C

\[
R\cdot + R-O-O\cdot \rightarrow R-O-O-R
\]

bound C-O-O-C

\[
2 R-O-O\cdot \rightarrow R-O-O-R + O_2
\]

induction

mostly photooxidation and enzymatic reaction

singlet oxygen

hydroperoxide, first radicals forming due to decomposition of hydroperoxides

decomposition of hydroperoxides

monomolecular decomposition

\[
R-O-O-H \rightarrow R-O\cdot + \cdot OH \text{ and } R-O-O-H \rightarrow R-O-O\cdot + \cdot H
\]

alkoxy radical as a new species

bimolecular decomposition (at higher concentration ROOH)

\[
2 R-O-O-H \rightarrow R-O-O\cdot + R-O\cdot + H_2O
\]

reactivity of radicals

\[HO\cdot > R-O\cdot > R-O-O\cdot\]

fate of alkoxy radicals

decomposition \(\rightarrow\) aromatic compounds

recombination in terminal stage
oxidation of unsaturated acids (at ordinary temperature)

\[ \text{O : L : LL} = 1 : 10 : 100 \]

<table>
<thead>
<tr>
<th>Structure</th>
<th>Dissociation energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-CH₂-</td>
<td>422</td>
</tr>
<tr>
<td>CH₃-CH-H-</td>
<td>410</td>
</tr>
<tr>
<td>-H-CH-CH=CH-</td>
<td>322</td>
</tr>
<tr>
<td>-CH=CH-CH-CH=CH-</td>
<td>272</td>
</tr>
</tbody>
</table>

oxidation of saturated acids (at elevated temperature)

frying and roasting

**Mechanisms:** oxidation of oleic acid

→ mixture 4 hydroperoxides in ratio of cca 1:1:1:1

cis (or trans), trans - geometric isomers

oxidation of linoleic acid

→ mixture 7 hydroperoxides, mostly 9-a 13-

oxidation of linolenic acid
mixture of many hydroperoxides
mostly 9-, 12-, 13- and 16- with 2 conjugated double bonds and one isolated bond

**Subsequent reaction of hydroperoxides**

→ secondary autooxidation products

- same number C: epoxy-, hydroxy-, oxo-acids
- lower number C: aldehydes, hydrocarbons and others
- higher number C: different polymers

formation of epoxy-, hydroxy- a oxo-compounds

formation of aldehydes and hydrocarbons

general mechanisms

for example 9-hydroperoxy-10,12-fatty acid from linoleic acid
9-oxononanoic, octanoic, \((E,Z)\)-deca-2,4-dienal, \((Z)\)-non-3-enal,

**subsequent reaction of aldehydes**

**polymers formation**

- bond C-C
- ether bond
- peroxide bond

- two-fold C-C bond
- tetrahydrofurane bond
- C-C peroxide bound

- cyclopentane cycle

- two-fold bond C-C
- tetrahydropyrane bond
- dioxane bond

**reaction of oxidised lipids with proteins**

**oxidation with singlet oxygen**

- photooxidation (photosensitilisators)
- enzymatic reaction (photosynthesis)
addition on double bond, ~ 1000 times faster than autoxidation

\[
\begin{align*}
C_{18:1} & \rightarrow 9- \text{ a 10-hydroperoxid} \\
C_{18:2} & \rightarrow 9- \text{ a 13-hydroperoxid} \\
C_{18:3} & \rightarrow 9-, 12-, 13-, 16- \text{ a 10-, 15-,hydroperoxid}
\end{align*}
\]

compounds destroying singlet oxygen
- \( \beta \)-carotene and other carotenoides
- tocopherols
- ascorbic acid
- \(^1\) carotenoid + \(^1\)O\(_2\) \(\rightarrow\) \(^3\) carotenoid + \(^3\)O\(_2\)
- \(^3\) carotenoid (excited triplet state) \(\rightarrow\) \(^1\) carotenoid

**Enzymatic oxidation**

lipoxygenases (lipoxidases, linoleate: O\(_2\) oxidoreductase), \(E_{18:2} = 17 \text{ kJ/mol}\)

unsaturated. lipid \(\rightarrow\) hydroperoxides of unsaturated lipids (optically active)
specificity (regio-, stereo-)

example C\textsubscript{18:2}

soya $\rightarrow$ (13\textit{S}), 9-\textit{cis}, 11-\textit{trans}
tomatoes $\rightarrow$ (9\textit{S}), 10-\textit{trans}, 12-\textit{cis}
mushrooms $\rightarrow$ (10\textit{S}), 8-\textit{trans}, 12-\textit{cis}

negative, positive consequences

animals: decomposition by glutathioneperoxidases
plants and mushrooms: splitting by lyases, isomerases, aroma compounds

13-OOH-9,11,15-~

$\text{CH}_3\text{CH}=$

(Z)-hex-3-enal (green flavour)

(E)-hex-2-enal, leaf aldehyde, product of isomeration of (Z)-hex-3-enal by isomerases

oily, greasy, green smell

9-OOH-10,12,15-~

$\text{CH}_3\text{CH}=O$

(Z)-non-2-enal (oily smell)

10-OOH-8,12-~

$\text{CH}_3\text{CH}=$

(R)-okt-1-en-3-ol (mushroom-like smell)

\textbf{thermal reactions}

geometrical isomerisation \textit{cis}/\textit{trans}
positional isomerisation
cyclisation
polymerisation

Diels-Alder reaction (monoene C_{18:1} and diene C_{18:2})

mechanisms of oleic acid isomers formation (~270 °C)

inhibition of autooxidation

- temperature
- air
- radiation
- inhibitors (antioxidants, synergists)

antioxidants
classification according to origin

- natural (mostly tokopherols, phenols
- synthetic (mostly phenols)
classification according to activity (mechanisms)
- primary (reaction with s radicals)
- secondary (reduction of R-O-OH)

phenolic antioxidants (mechanism of action)

\[
R-O-O\bullet + H-A \rightarrow R-O-O-H + A\bullet
\]

![H-A (antioxidant)](image1)
![A\bullet (radical antioxidant)](image2)

main reactions

\[
2A\bullet \rightarrow A-A
\]

\[
A\bullet + R-O-O\bullet \rightarrow R-O-O-A
\]

\[
A\bullet + R-O\bullet \rightarrow R-O-A
\]

side reactions (> 0.01 %)

\[
A\bullet + O_2 \rightarrow A-O-O\bullet
\]

\[
A-O-O\bullet + R-H \rightarrow A-O-O-H + R\bullet
\]

main natural antioxidants

![tocopherols](image3)
![gallates](image4)

main synthetic antioxidants

![BHT](image5)
![BHA (isomers cca 9 : 1)](image6)
![TBHQ](image7)

applications

BHA, BHT, tocopherols, dodecylgallate

TBHQ, propylgallate

type of emulsion: oil/water

pure fats (oils)
evaluation of fat oxidation
induction period

P - peroxide number, t – time of autoxidation at 60 °C (days), 1 - concentration of antioxidants (BHA) = 0 %, 2 - 0.02 %, I_1 a I_2 = induction periods, protective factor PF = (I_2-I_1)/I_1