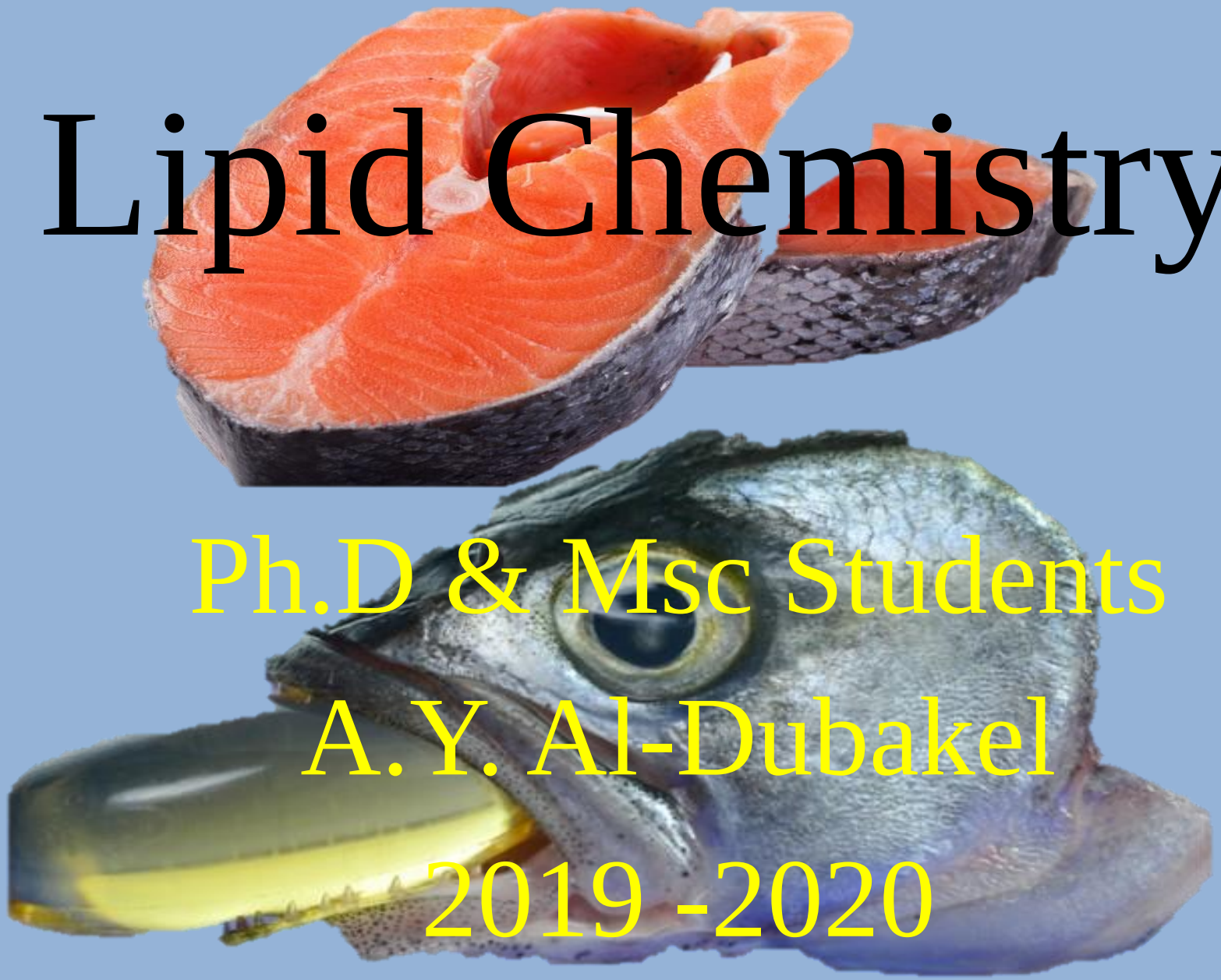
Lipid Chemistry



Ph.D & Msc Students

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Lecture 4

Lipid oxidation

There are three main steps

i. Initiation
ii. Propagation
iii. Termination

Lipid Oxidation

- **Initiation:**
  RH + O2 -->R· + ·OH
  R· + O2 --> · + ROO·

- **Propagation:**

  ROO· + RH --> R· + ROOH
  ROOH--> RO· + HO·

- **Termination:**

  R· + R· --> RR
  R· + ROO·--> ROOR
  ROO· + ROO· --> ROOR + O2

i. Initiation

The initiation occurs by direct attack of oxygen in its most stable form on double bonds of fatty acids (RH).

The presence of a double bond in the fatty acid (RH) weakens the C-H bonds on the carbon atom adjacent to the double bond and so makes H removal easier.

Oxygen attack at the end carbon of the double bond and forms hydrogen peroxide.

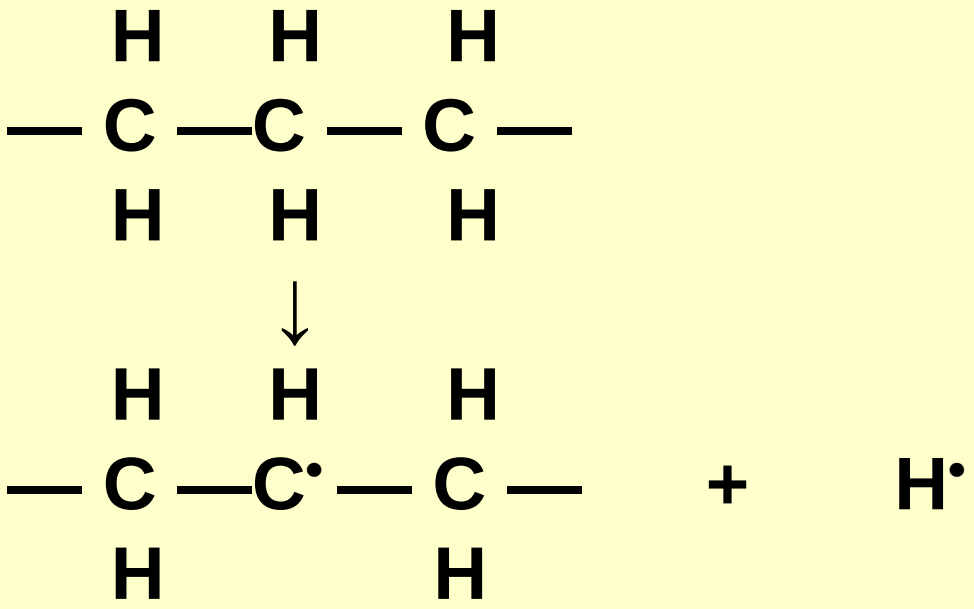
Hydroperoxides breakdown in several steps to form free radicals.

Initiator

RH $+O_2$ → ROOH → Free radicals ($R^{\bullet}$, $ROO^{\bullet}$)

Free radical mechanism

A free radical an atom lost an electron and left a with odd number of unpaired electrons.



When initiated two free radicals are formed. These radicals are very reactive and generally do not have long life time.

ii. Propagation

- Once the initial radicals have formed, the formation of other radicals proceeds rapidly.
- The new radicals will not be at the double bond. To remove a hydrogen from a double bond requires 80 Kcal/mole.
- To remove a hydrogen alpha to a double bond only requires 15 Kcal/mole.
- As a peroxyl radical is able to abstract H from another lipid molecule (adjacent fatty acid), especially in the presence of metals such as copper or iron, thus causing an autocatalytic chain reaction.
- The peroxyl radical combines with H to give a lipid hydroperoxide (or peroxide).
- This reaction characterizes the propagation stage.

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

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

iii) Termination

Any kind of alkyl radicals (lipid free radicals) **R•** can react with a lipid peroxide **ROO•** to give non-initiating and

Non-propagating species such as the relatively stable dimers **ROOR** or two peroxide molecules combining to form hydroxylated derivatives (ROH).

$R^{\bullet} + R^{\bullet} \rightarrow R\text{-}R$

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

$2ROO^{\bullet} \rightarrow ROO\text{-}OOR$

https://www.slideshare.net/GYANDEEP17/fatty-acid-oxidation-and-antioxidant-gyans24-04-18

Effects of Lipid Oxidation in Foods

- When lipids in food are oxidised, some of the product formed impart odour and flavours, usually undesirable, to the food.
- The free radicals generated during the oxidation reaction and some of the molecules formed when oxidized compound decombos (aldehydes, acids, alcohols, ketones etc.) can interact with and alter other constituents including pigments, vitamins, proteins and amino acids.
- These interactions can result in colour, texture and nutritive value.
- If foods containing oxidized lipids are consumed, the oxidation products could be involved in reactions leading to pathological changes.
- For e.g. malonaldehyde and oxidation product of certain polyunsaturated fatty acids found in many foods, is a potential carcinogen.

Pro-Oxidants

- Transition metals, particularly those possessing two or more valency states and a suitable oxidation reduction potential between them are effective pro-oxidants.
- e.g.copper, iron, manganese, cobalt and nickel
- If present even at very low concentrations(0.1ppm) can decrease the induction period and increase the rate of oxidation.
- Trace metals are naturally occurring in all food tissues and all fluids of biological origin (eggs, milk and fruit juices) and they are present in both free and bound forms.
- Heme compounds are also important pro-oxidants.