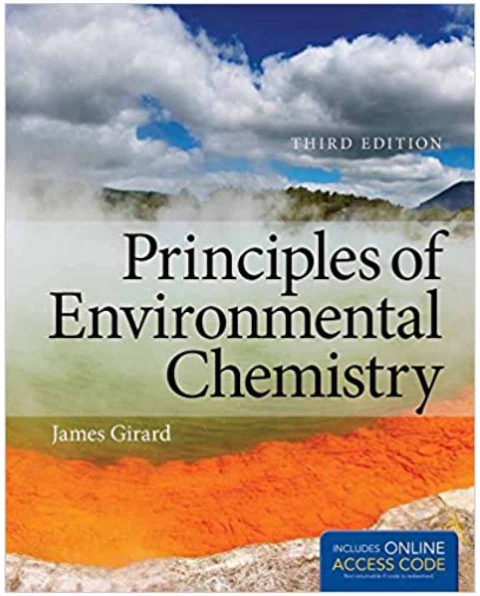
CY-1018: Environmental Chemistry Theory

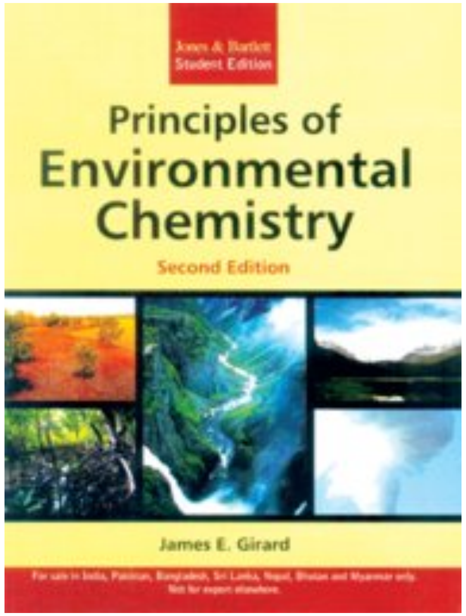
Know our environment (chemistry of lithosphere, energy balance, sustainability and recycle), Know about global warming (infrared absorption, molecular vibration, atmospheric window, residence time of greenhouse gases, evidences and effects of global warming), Deeper analysis of atmospheric pollution (Chemistry of CO, NOx, VOCs, SO_2, Industrial smog, photochemical smog), Ozone depletion (production, catalytic destruction),

Organic Chemicals in the Environment, Insecticides, Pesticides, Herbicides and Insect Control, Soaps, Synthetic Surfactants, Polymers, and Haloorganics. Fate of organic/inorganic chemicals in natural and engineered systems (fate of polymers after use, detergents, synthetic surfactants insecticides, pesticides etc. after use),

Aspects of transformations in atmosphere (microbial degradation of organics-environmental degradation of polymers, atmospheric lifetime, toxicity). Green Chemistry and Industrial Ecology.

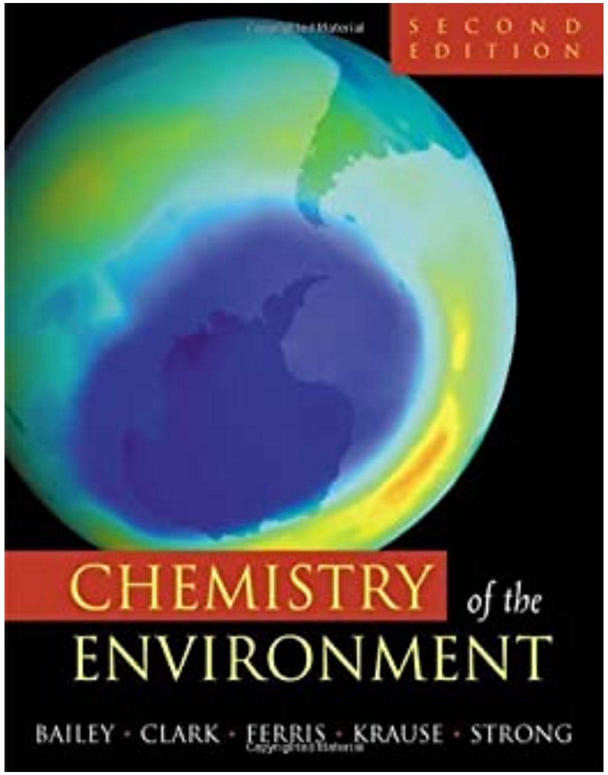
Future challenges (CO_2 sequestering, Nuclear energy). A project on environment related topic.





Principles of Environmental Chemistry
By James E. Girard

Chemistry of the Environment, Second Edition by R. A. Bailey, H. M. Clark, J. P. Ferris, S. Krause, R. L. Strong



Microbial degradation of organics

Environmental degradation of polymers

Biodegradation is the breakdown of organic matter by microorganism

Bioremediation : use of either naturally occurring or deliberately introduced microorganisms to consume and break down environmental pollutants

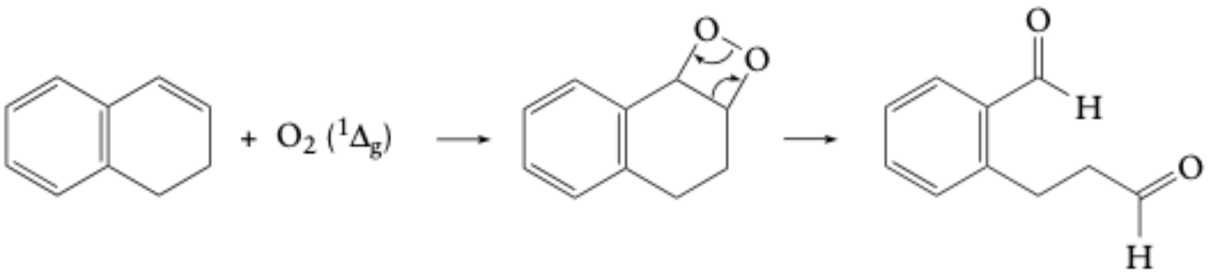
Oil Spill


Amoco Cadiz
1,619,048 bbl
1978
Odyssey
1,023,809 bbl
1988
Mingbulak
2,000,000 bbl
1992
Deepwater Horizon
4,900,000 bbl *
2010
MT. Haven
1,065,600 bbl
1991
Lakeview Gusher
9,000,000 bbl
1910
Ixtoc
3,333,333 bbl
1979
Atlantic Empress
2,123,800 bbl
1979
Gulf War
11,000,000 bbl
1991
ABT Summer
1,924,000 bbl
1991
Castillio de Bellver
1,864,800 bbl
1983
Well - Land
Well - Ocean
Ship
War
* Estimated July 15, 2010 (assumes 60,000 bbl per day)

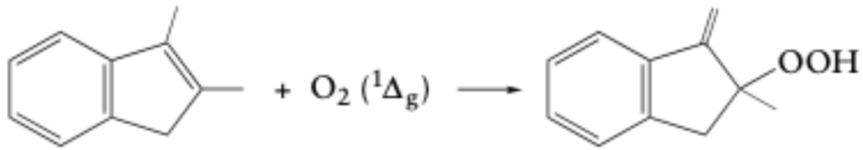

The Guardian

6.4.1 Weathering of an Oil Spill

The polycyclic aromatic hydrocarbons in crude oil sensitize the photochemical formation of singlet oxygen (Section 5.2.2), which oxidizes the olefins present to cyclic dioxides and hydroperoxides:

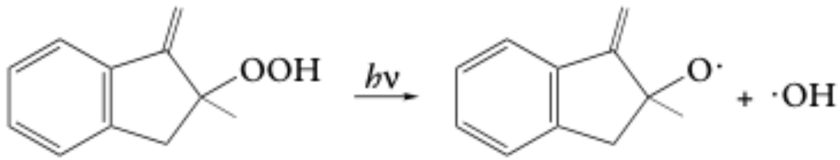


(6-1)



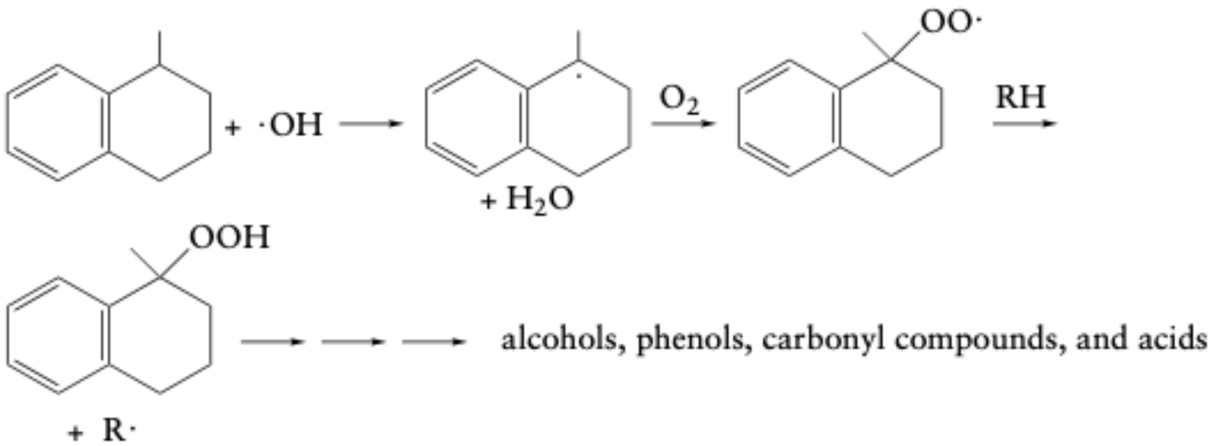
(6-2)

These compounds can either rearrange directly [equation 6-1] or be cleaved photochemically to form hydroxyl radicals



(6.3)

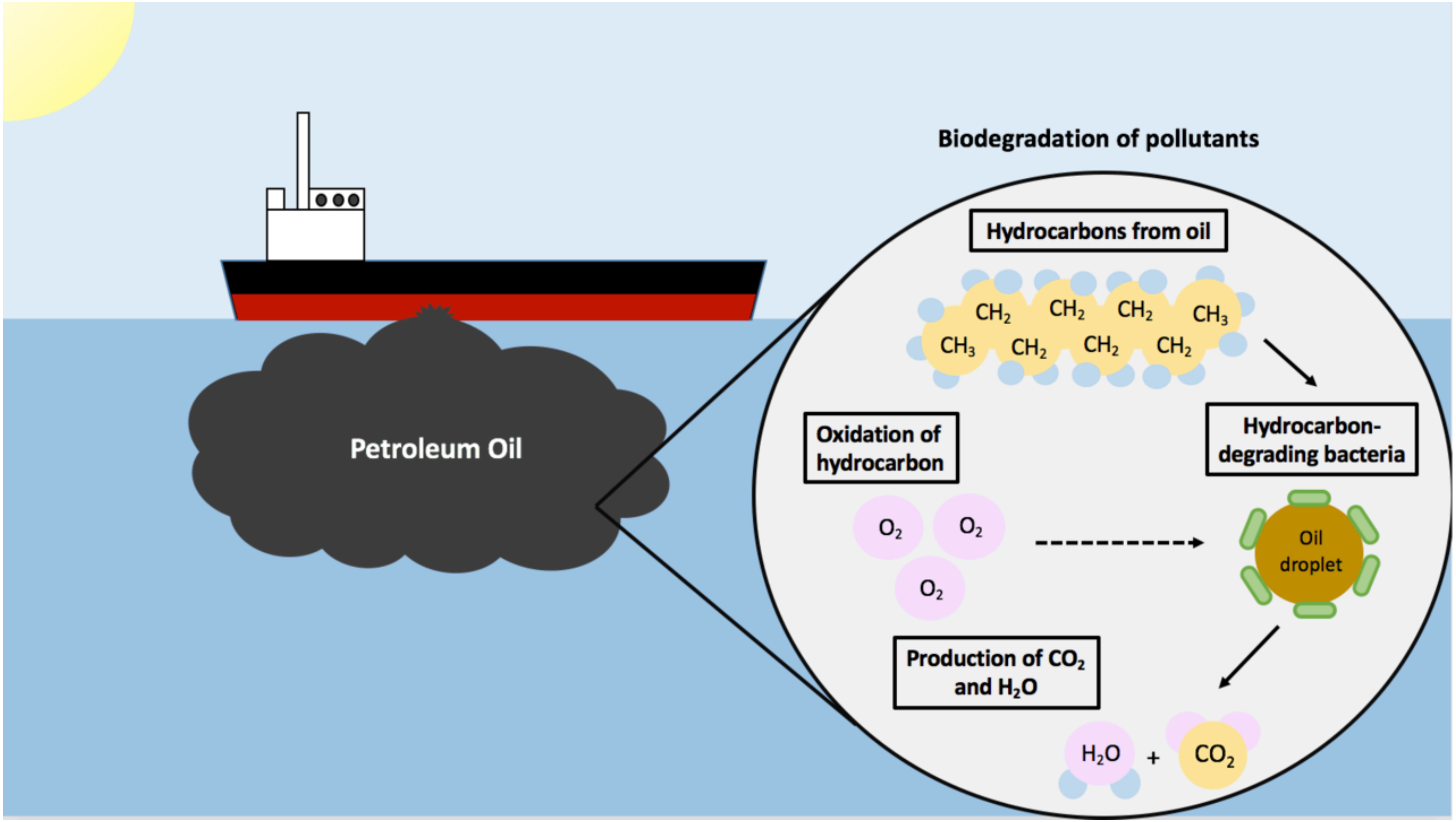
that attack the other unsaturated molecules present:



(6.4)

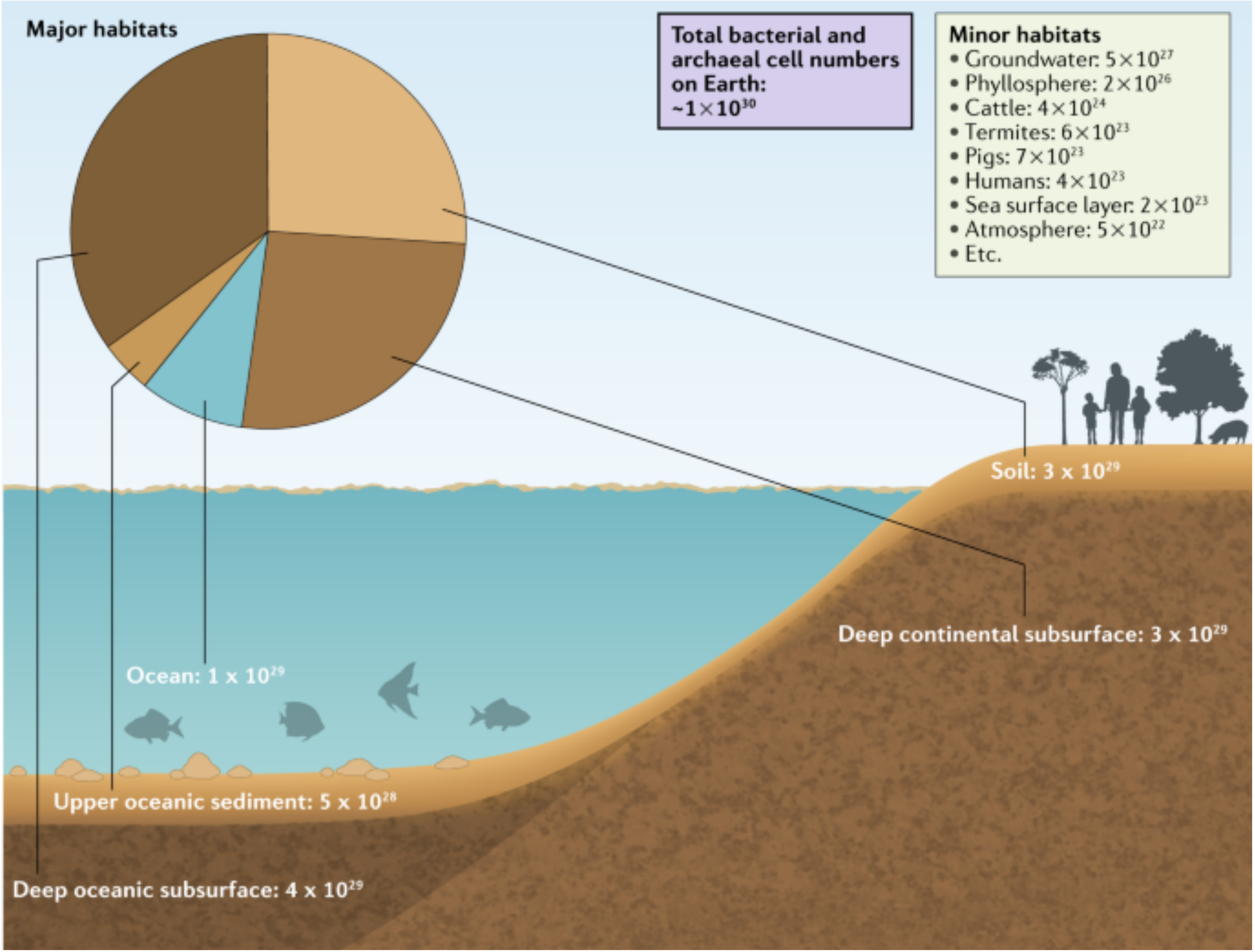
- The breakup of the spill is slowed if it is washed up on the shore.
- Dispersal and degradation will continue if there is a strong wind and surf,
- but oil spills in quiet bays or lagoons may take 5-10 years to disperse in the absence of wave and wind action.
- The toxic effects on marine life likewise persist for 5-10 years in these environments

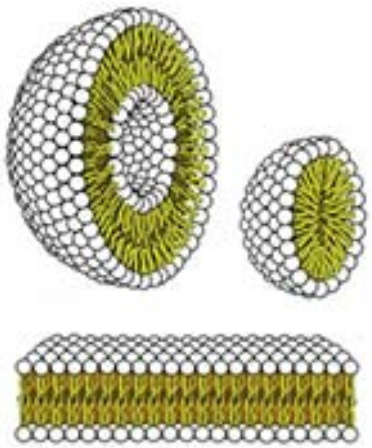
Microorganisms eat this Oil



Petroleum Oil
Biodegradation of pollutants
Hydrocarbons from oil
CH2 CH2 CH2 CH3
CH3 CH2 CH2 CH2
Hydrocarbon-degrading bacteria
Oil droplet
Oxidation of hydrocarbon
O2
O2
O2
Production of CO2 and H2O
H2O + CO2

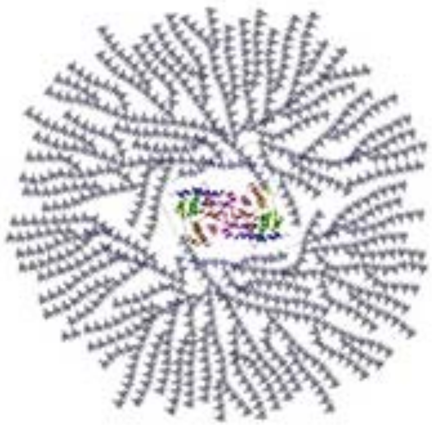

Bacteria Everywhere on Earth
Soil
Ocean
Air
Desert


Major habitats
Total bacterial and archaeal cell numbers on Earth: ~1×10^30
Minor habitats
• Groundwater: 5×10^27
• Phyllosphere: 2×10^26
• Cattle: 4×10^24
• Termites: 6×10^23
• Pigs: 7×10^23
• Humans: 4×10^23
• Sea surface layer: 2×10^23
• Atmosphere: 5×10^22
• Etc.
Soil: 3 x 10^29
Deep continental subsurface: 3 x 10^29
Ocean: 1 x 10^29
Upper oceanic sediment: 5 x 10^28
Deep oceanic subsurface: 4 x 10^29



LIPIDS

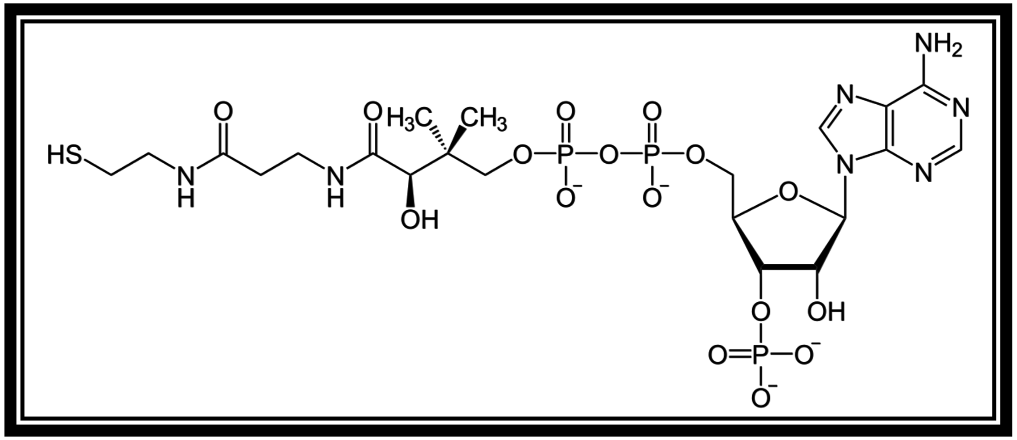
NUCLEIC ACIDS

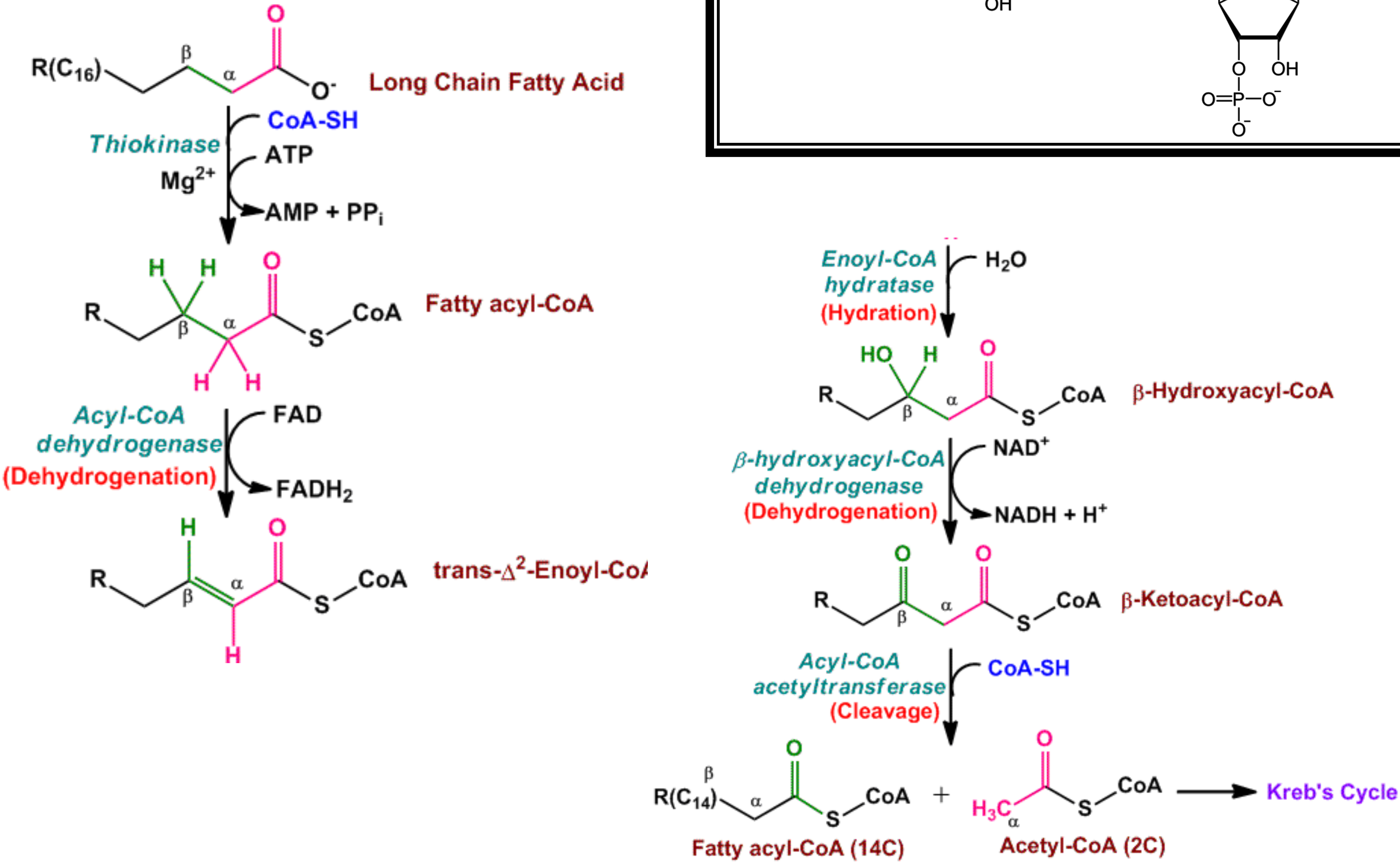


CARBOHYDRATES

PROTEINS

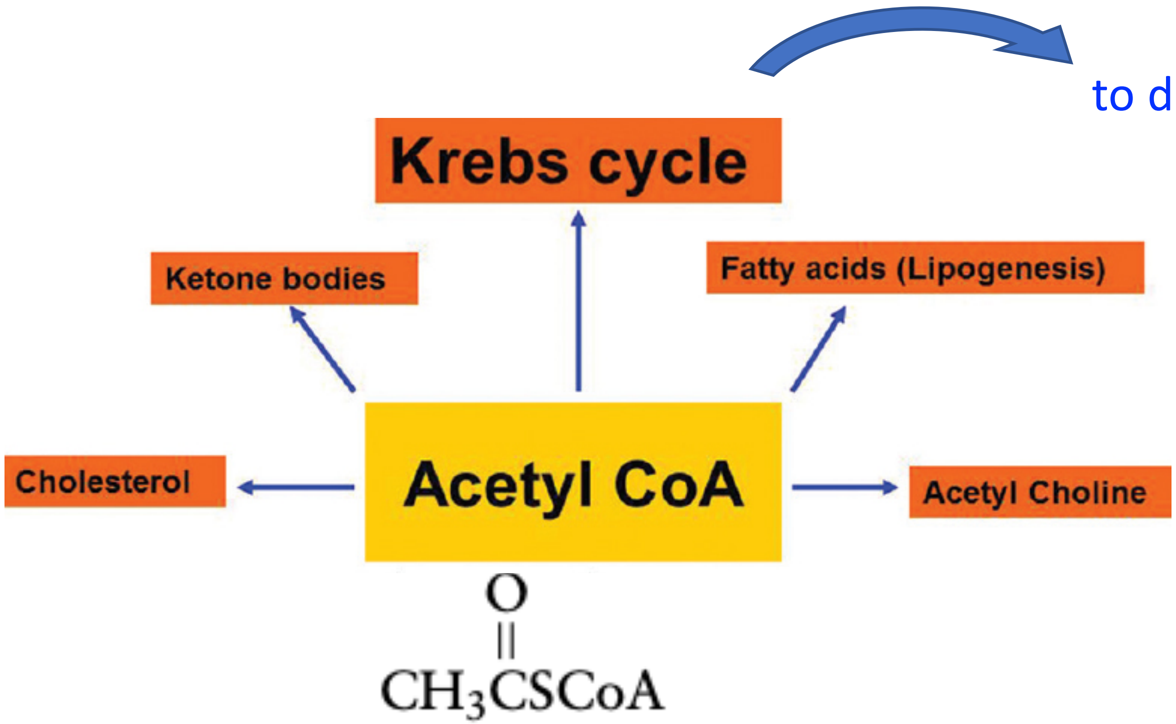
β- oxidation procedure





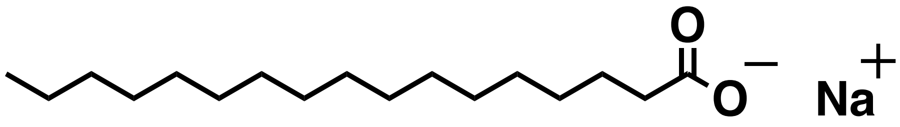
oxidatively degraded to CO_2 and H_2O

provide the energy needed
to drive microbial metabolic processes



The rate of degradation by other environmental reagents such as sunlight, oxygen, or water is much slower than that of microbial degradation

Soaps



Synthetic surfactants

$R{-}SO_3^-\ Na^+$ **Alkyl sulfonates**

$$[CH_3(CH_2)_n\overset{\displaystyle CH_3 \atop |}{C}HOSO_3^-Na^+$$

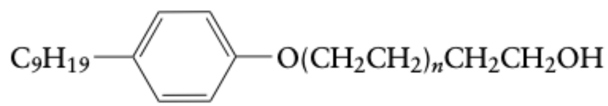
Alcohol sulfate

$$RO(CH_2CH_2CH_2)_nCH_2CH_2OSO_3^-Na^+$$

Alcohol ether sulfate

Non-ionic Alcohol ethoxylates RO(CH2CH2)n CH2CH2OH

Alkylphenol ethoxylates R-(p-benzene)-O(CH2CH2)n CH2CH2OH



The microbial breakdown of detergents and petroleum

requires the terminal oxidation of the hydrocarbon chain to a carboxylic acid

followed by the β- oxidation procedure

This terminal oxidation is a well-documented process,

Molecular oxygen is the oxidizing agent, and the oxygen is activated by binding to the iron-containing enzyme cytochrome P-450

(function as Monooxygenases)

$$RCH_2CH_2CH_3 \xrightarrow{[O]} RCH_2CH_2CH_2OH \xrightarrow{[O]} RCH_2CH_2CO_2H \xrightarrow{[O]} R_2CO_2H + CH_3CO_2H$$

but are slow, especially with high molecular weight materials that do not readily pass through the microbial cell wall

- Fatty acids (including protonated soaps) occur widely in biological systems and are therefore readily degraded by microorganisms in enzyme-catalyzed reactions.

- Linear hydrocarbons and linear detergents are similar in structure to soaps, and these are degraded in the same or similar pathways.

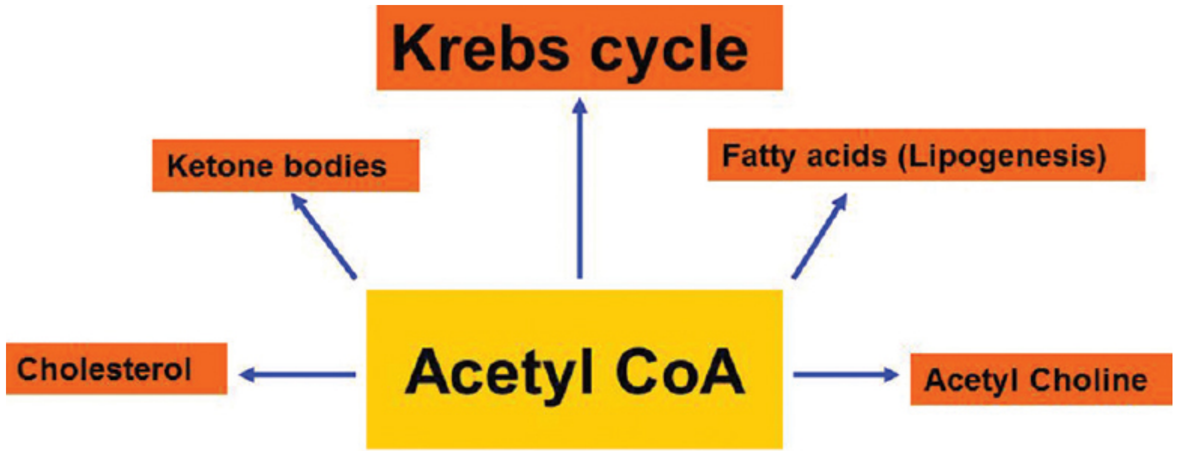
$$RCH_2CH_2CO_2H + CoASH \longrightarrow RCH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}SCoA$$

$$RCH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}SCoA + FAD \longrightarrow RCH{=}CH\overset{\overset{\displaystyle O}{\|}}{C}SCoA + FADH_2$$

$$RCH{=}CH\overset{\overset{\displaystyle O}{\|}}{C}SCoA + H_2O \longrightarrow R\overset{\overset{\displaystyle OH}{|}}{C}HCH_2\overset{\overset{\displaystyle O}{\|}}{C}SCoA$$

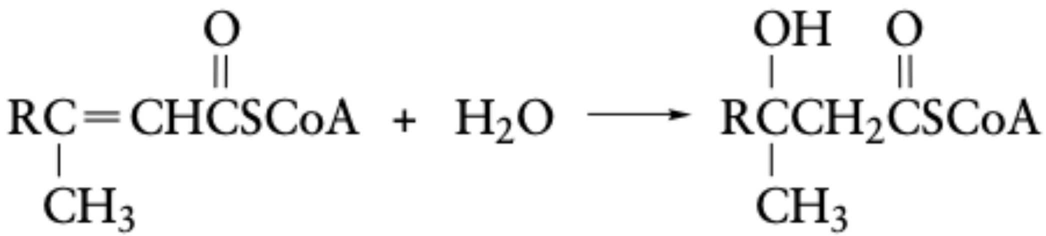
$$R\overset{\overset{\displaystyle OH}{|}}{C}HCH_2\overset{\overset{\displaystyle O}{\|}}{C}SCoA + NAD^+ \longrightarrow R\overset{\overset{\displaystyle O}{\|}}{C}CH_2\overset{\overset{\displaystyle O}{\|}}{C}SCoA + NADH + H^+$$

$$R\overset{\overset{\displaystyle O}{\|}}{C}CH_2\overset{\overset{\displaystyle O}{\|}}{C}SCoA + H_2O \longrightarrow R\overset{\overset{\displaystyle O}{\|}}{C}OH + CH_3\overset{\overset{\displaystyle O}{\|}}{C}SCoA$$



branching in the alkyl chain of **alkylbenzene sulfonate (ABS)** detergents

impeded specific steps in reactions: slow environmental degradation



microorganisms are able to get around these simple barriers

either by oxidatively removing the methyl groups

or by cleaving off propionyl CoA [CH3CH2C(O)SCoA] in place of acetyl CoA

Surfactants: structural diversity: difficult to formulate guidelines for biodegradation and the need to ``acclimate'' the bacteria population

Guidelines to facilitate understanding of the microbial degradation of LAS and ABS detergents

1. Highly branched detergents degrade slowly in part

2. The ease of cleavage of the surfactant increases, the further the polar sulfate or sulfonate grouping is from the alkyl terminus of the chain.

   Consequently, surfactants with branched chains that are shorter than those with linear chains containing the same number of carbon atoms degrade more slowly.

   Possible related to the ease of binding of the surfactant to a degradative enzyme

3. Rate of degradation of surfactants is slower in concentrated sol. than in dilute sol.

   suggests that minor constituents of the surfactant mixture inhibit the microbial degradative enzymes

These guidelines also apply to the alkyl substituent of the **alkyl- and alkyl- phenol ethoxylates**

1. The alkyl chain will degrade slowly if it is highly branched, and then the ethoxylate grouping will degrade

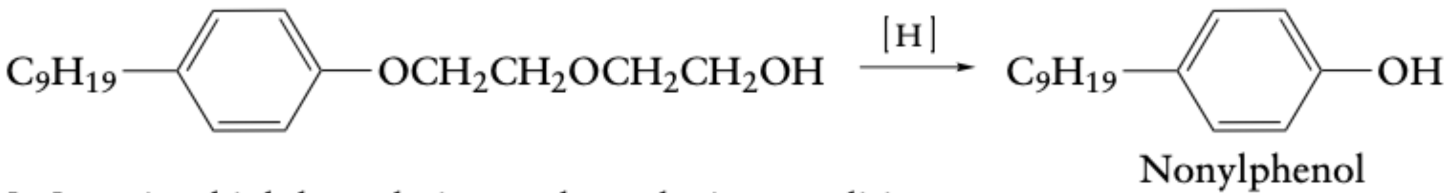
2. The rate of degradation of the alkyl chain decreases as the number of ethoxylate groups increases.

   the extent of degradation of the ethoxylate chain of an alkylphenol ethoxylate decreases as the number of ethoxylate groupings increase from 5 to 20.

   increased difficulty of transport of the more hydrophilic detergent (with more ethoxylate groupings) through the hydrophobic cell membrane of microorganisms.

3. The alkylphenol ethoxylates degrade more slowly than the alcohol ethoxylates

   sometime the partial degraded compound ppt out at waste disposal and its anaerobic degradation product (Nonlyphenol) is toxic



[H] = microbial degradation under reducing conditions

Biodegradation pathway of ethoxylate surfactants has not been determined,

some insight into the mechanism can be obtained from studies on the degradation of glycols and simple ethoxylate oligomers shown in reaction

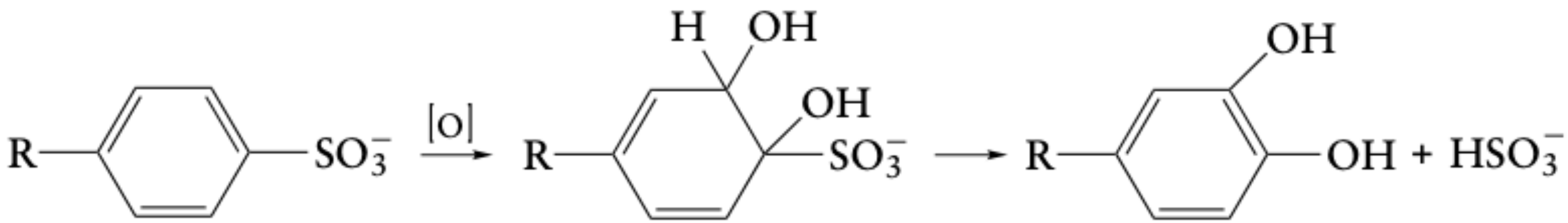
$$\mathrm{ROCH_2CH_2OH} \xrightarrow{[O]} \mathrm{RO\overset{\overset{HO}{|}}{C}HCH_2OH} \xrightarrow{[O]} \mathrm{RO\overset{\overset{HO}{|}}{C}H\overset{\overset{O}{\|}}{C}H} \xrightarrow{[O]} \mathrm{RO\overset{\overset{HO}{|}}{C}H\overset{\overset{O}{\|}}{C}OH} \longrightarrow$$

$$\mathrm{ROCH_2OH} + \mathrm{CO_2} \xrightarrow{[O]} \mathrm{RO\overset{\overset{O}{\|}}{C}H} \xrightarrow{H_2O} \mathrm{ROH} + \mathrm{H\overset{\overset{O}{\|}}{C}OH}$$

$R = \mathrm{HOCH_2CH_2OCH_2CH_2O^-}$, where [O] indicates oxidation.

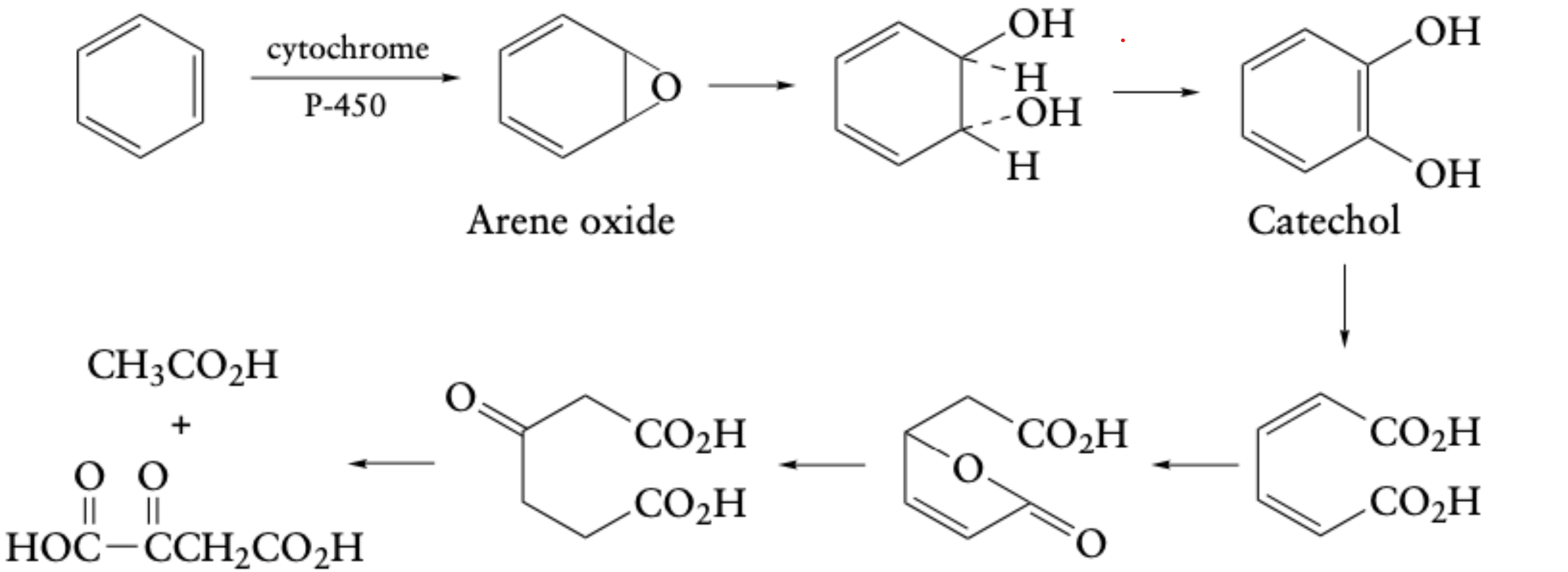
The sulfate esters in alcohol sulfates are readily hydrolyzed by microbial sulfatase enzymes. Sulfonates present in the surfactants are subject to rapid oxidative elimination by a variety of aquatic bacteria

$$\mathrm{RCH_2SO_3^-} \xrightarrow{[O]} \mathrm{R\overset{\overset{OH}{|}}{C}HSO_3^-} \longrightarrow \mathrm{RCHO} + \mathrm{HSO_3^-}$$

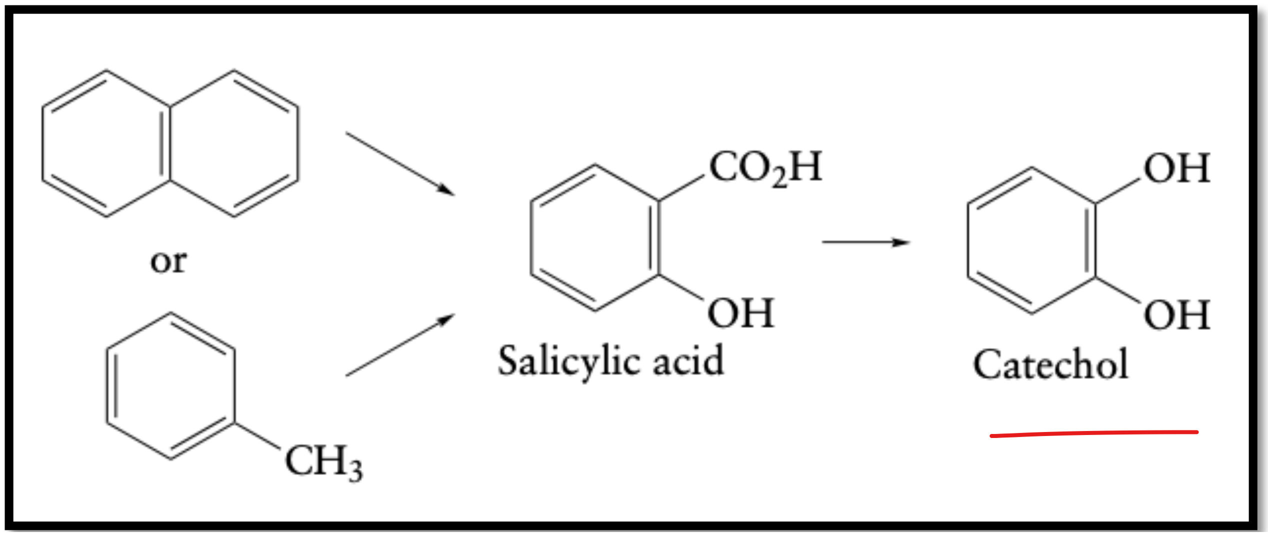


sulfonate groups do not slow the environmental degradation of the alcohol sulfates

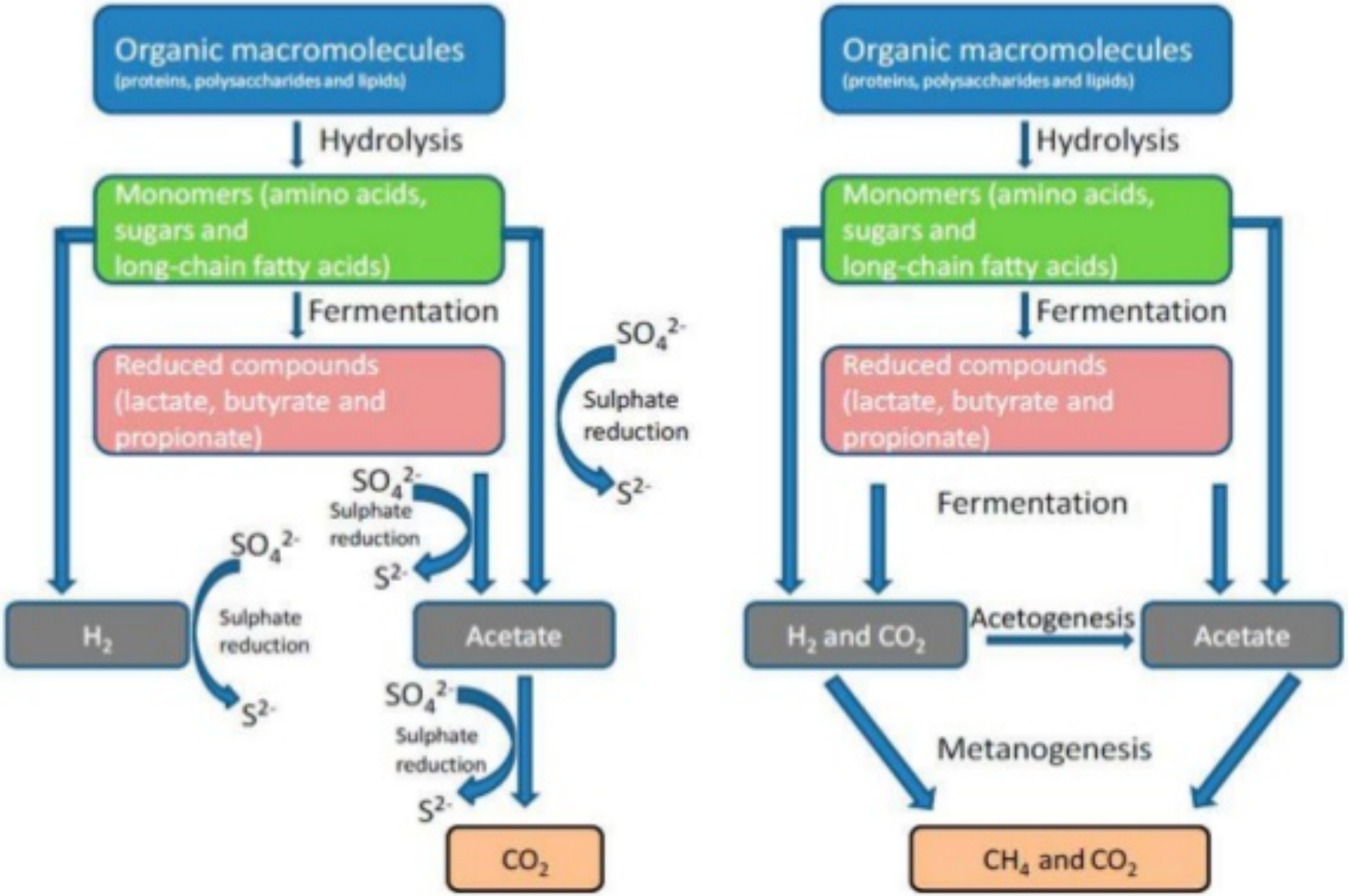
- The microbial oxidation of the cyclic hydrocarbons and aromatic compounds present in detergents and petroleum is also catalysed by the enzyme cytochrome P-450 in microorganisms.

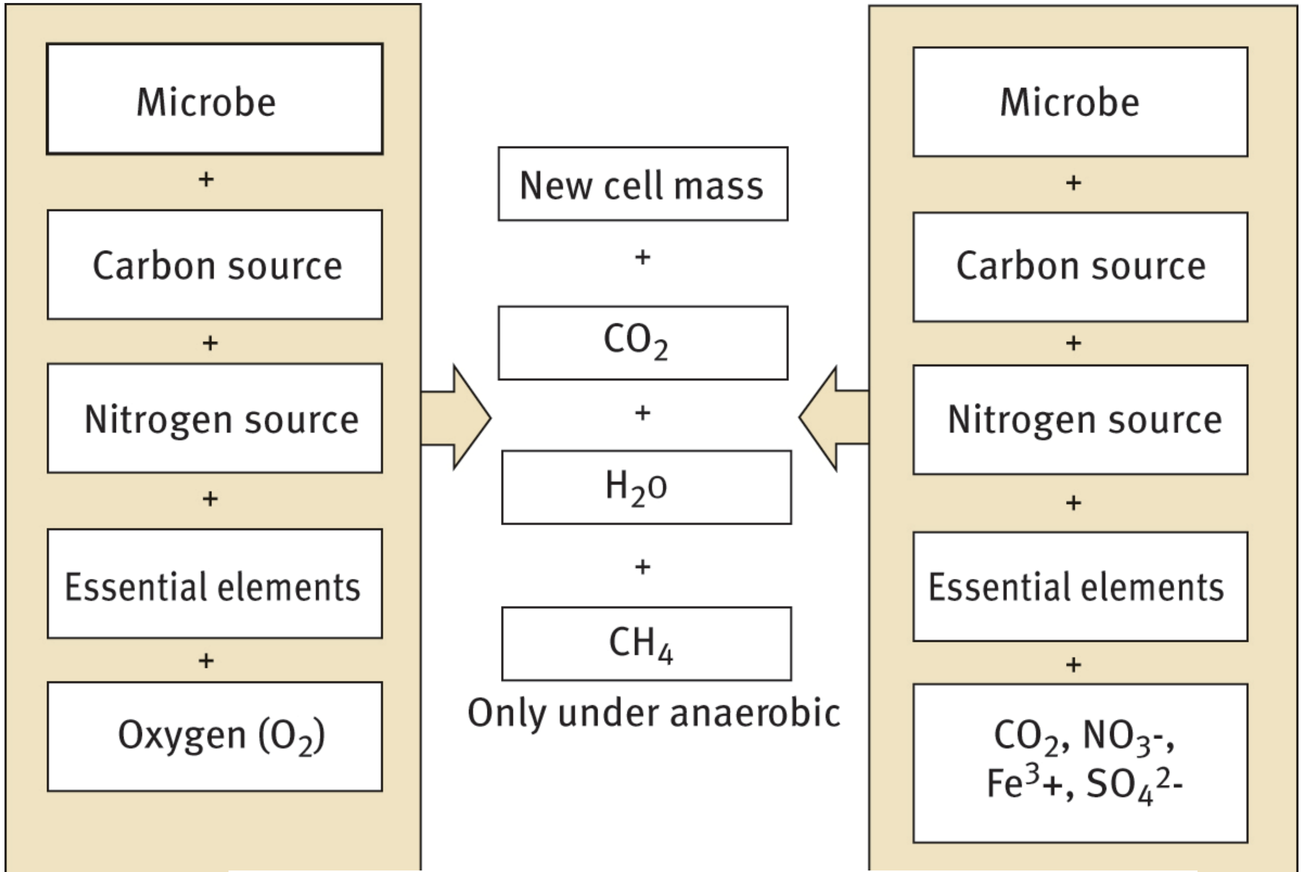


more highly condensed aromatics proceeds via salicylic acid



AEROBIC & ANAEROBIC BIODEGRADATION OF ORGANIC COMPOUNDS





AER

AEROBIC	ANAEROBIC
Most rapid and fast degradation .	Time consuming and slow
No pungent gas produced .	Pungent gas produced.
More expensive	Less expensive
Large disposable waste generated.	Less waste is generated
Microbes are *Xanthomonas,Coma monas*	*Clostridia ,Eubacteria etc.*