CY1018: Environmental Chemistry Theory

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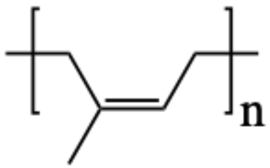
Microbial degradation of organics

Environmental degradation of polymers

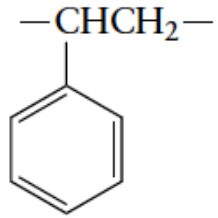
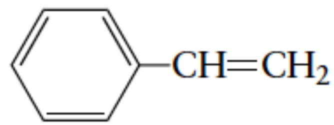
Natural rubber is not easily biodegradable



***cis*-1,4- polyisoprene**

Proteins: polymers of amino acids

Starch and Cellulose: polymers of sugars

Polymer	Repeat unit	Monomer(s)
Polyethylene	$-CH_2CH_2-$	$H_2C{=}CH_2$
Polypropylene	$-CH(CH_3)CH_2-$	$CH_3HC{=}CH_2$
Polystyrene		

- Globally, only 18% of plastics waste are recycled, and 24% are incinerated
- 58% is placed in landfills (dumping yards)
- Relatively little decomposition takes place in landfills, so very little of this plastic material disappears with time (stable for more than 500 years)

- Biodegradable Polymers

water-soluble polymers : Polymers that tend to be used only once

Microorganisms use degradable polymers for their growth

- Many hydrocarbon polymers have chemical reactivity similar to that of high boiling petroleum fractions

Environmental Degradation of Polymers

Nonbiodegradable Polymers

- ❖ **Goal of the polymer chemist was to design a polymer that degrades very slowly**
  - ❖ use in vinyl siding for homes : should be resistant to light air, water etc

    May appear to degrade but actually due to the loss of their phthalate ester plasticizer

    vinyl products become brittle and crack, but the actual degradation of the the polymer proceeds more slowly.

Photooxidation

Polymers will be degraded if they absorb sunlight at wavelengths greater than that of the radiation that is not absorbed by stratospheric ozone

Direct photolysis is not usually a major degradative pathway

Most polymers do not have functionality that results in light absorption at wavelengths greater than 290 nm,

- Indirect photochemical processes, such as oxidation by photochemically generated singlet oxygen can also result in polymer degradation

$$R{-}R \xrightarrow{\text{mechanical shearing}} 2R^{\cdot}$$

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

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

Radical formed by polymer processing

Hydroperoxides absorb light at wavelengths greater than 290nm and are cleaved to hydroxyl radicals and alkoxy radicals or alternatively cleave to carbonyls

$$ROOH \xrightarrow{h\nu} RO^{\cdot} + {}^{\cdot}OH$$

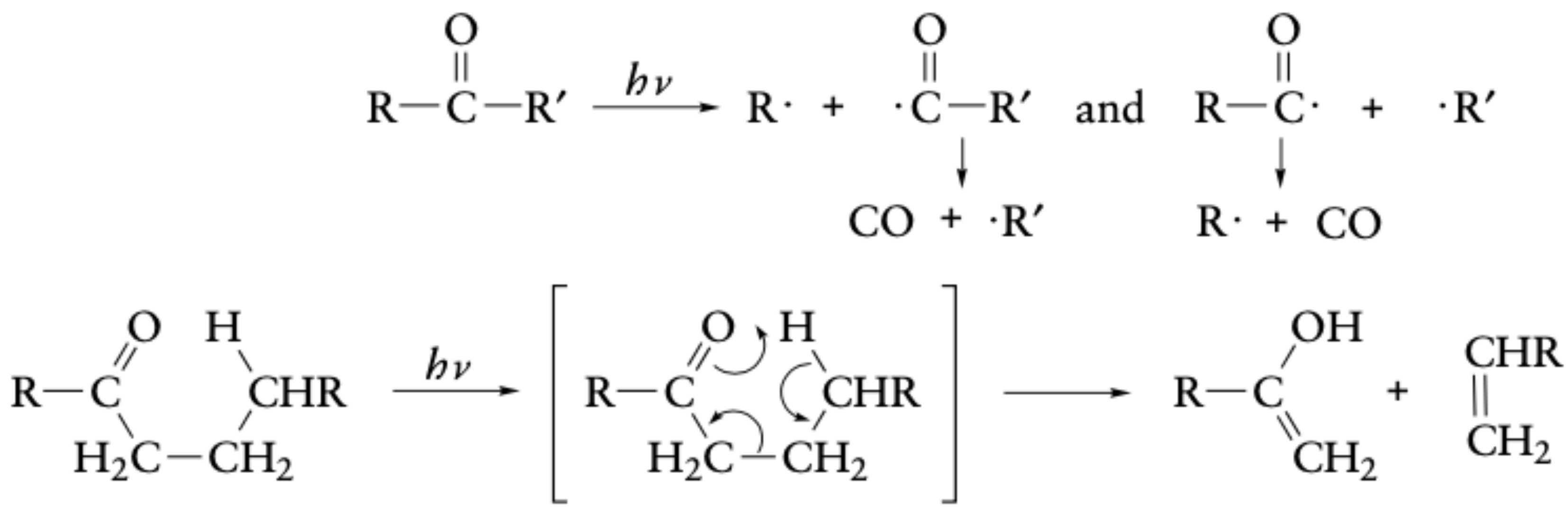
$$ROOH \xrightarrow{h\nu} R'(CO)R'', R'''(CO)CH_3$$

Presence of iron (III) or Titanium (IV) impurities can also trigger the same radical processes

- Antioxidants, which react with free radicals, are added to many polymers to slow their rate of degradation

Photochemical decomposition Triggered by Carbonyl Groups

absorb UV light at 300-325nm and initiate reactions leading to the cleavage of the polymer backbone: Norrish Type I and Norrish Type II



- Polymers have been prepared in which carbonyl groups were purposely incorporated into the chain to facilitate their extensive photochemical degradation.

  - Poly- styrene cups in which 1% of the styrene units also contained a ketone grouping broke down to a wettable powder after standing outside in the sun for 3 weeks

    NOT COMPLETELY DEGRADED BUT FRAGMENTED
  - copolymer of ethylene and carbon monoxide is being used to make the plastic strap that holds beverage cans

Biodegradation

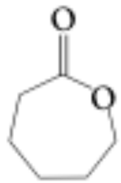
most of the biodegradable polymers contain functional groups that are subject to attack by microbial enzymes

contain ester or amide groups that can be hydrolyzed or linear chains that can be oxidatively cleaved

Problem: inability of microorganisms to ingest high polymers through their cell walls
500 Da

- Some microorganisms that degrade polyesters secrete esterases, enzymes that catalyze the hydrolysis of ester groups, which break the polymer into smaller fragments that can then be ingested.

Some typical polymers that are biodegradable under aerobic conditions

Polymer	Repeat unit	Monomer(s)
Poly(vinyl acetate)	$\begin{array}{c} CH_3 \\ \vert \\ C{=}O \\ \vert \\ O \\ \vert \\ -CH_2CH- \end{array}$	$\begin{array}{c} CH_3 \\ \vert \\ C{=}O \\ \vert \\ O \\ \vert \\ H_2C{=}CH \end{array}$
Poly(vinyl alcohol)	$\begin{array}{c} OH \\ \vert \\ -CH_2CH- \end{array}$	
Poly(ethylene oxide)	$-CH_2CH_2O-$	$H_2C\overset{O}{-}CH_2$
Polyglycolate	$-OCH_2\overset{O}{\overset{\Vert}{C}}-$	$HOCH_2CO_2H$
Polylactate	$-O\underset{CH_3}{\underset{\vert}{C}}H\overset{O}{\overset{\Vert}{C}}-$	$HO\underset{CH_3}{\underset{\vert}{C}}HCO_2H$
Poly(β-hydroxybutyrate)	$-O\underset{CH_3}{\underset{\vert}{C}}HCH_2\overset{O}{\overset{\Vert}{C}}-$	$HO\underset{CH_3}{\underset{\vert}{C}}HCH_2CO_2H$
Poly(β-hydroxyvalerate)	$-O\underset{CH_2CH_3}{\underset{\vert}{C}}HCH_2\overset{O}{\overset{\Vert}{C}}-$	$HO\underset{CH_2CH_3}{\underset{\vert}{C}}HCH_2CO_2H$
Polycaprolactone	$-O(CH_2)_5\overset{O}{\overset{\Vert}{C}}-$	

Poly β-hydroxybutyrate (PHB) and the copolymer of β-hydroxybutyrate and β-hydroxyvalerate (PHBV) are unique in that they are synthesized by microorganisms

It has been possible to induce the microorganisms to prepare the copolymer PHVB by adding some b-hydroxyvalerate to their growth medium.

In 1999 it was reported that a genetically engineered plant (oilseed rape) produced PHVB directly. This process is not economically feasible at present

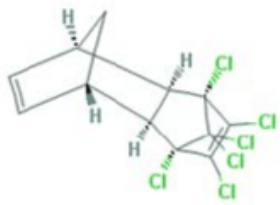
A polyethylene containing 5-20% starch granules is used in the manufacture of shopping bags that are claimed to be biodegradable.

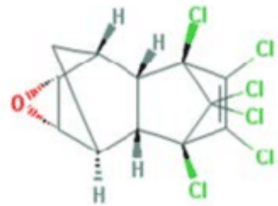
Other additives such as transition metals may also be added to the polyethylene to enhance the photodegradation of the polyethylene via hydroperoxides

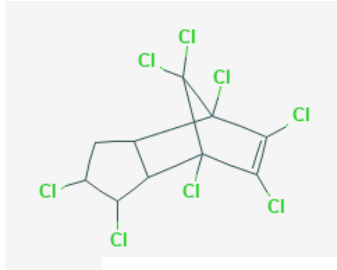
Organic Chemicals in the Environment

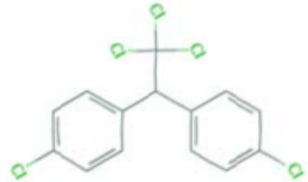
- pharmaceutical agents
- Fibers
- building materials
- agricultural chemicals
- solvents
- cleaning agents

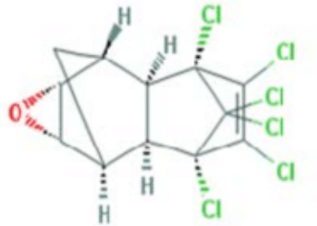
➢ inexpensive to manufacture
➢ used in large quantities

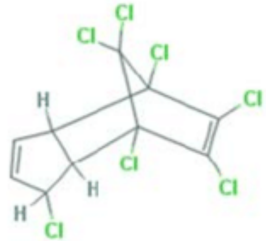

Aldrin


Dieldrin

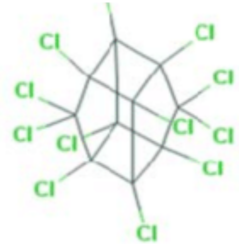

Chlordane

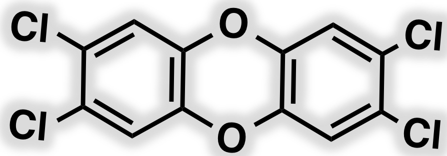

DDT

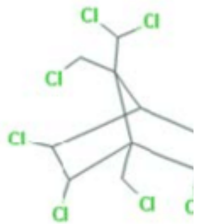

Endrin

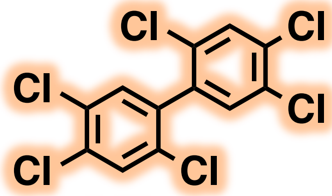

Heptachlor

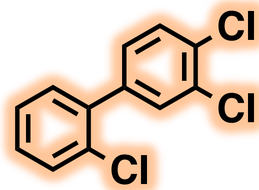

HCB

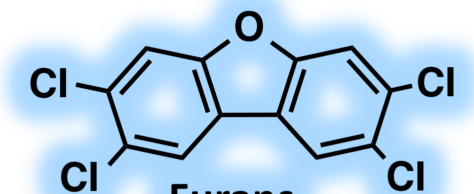

Mirex


Dioxins


Toxaphene


PCB_1


PCB_2


Furans

Polychlorinated compounds

2,3,7,8-tetrachlorodibenzo[*b*,*d*]furan

Stockholm Convention **In 2001**

The 12 Key POPs—the Dirty Dozen

POP	Use
Aldrin	crop insecticide (corn, cotton)
Chlordane	crop insecticide (vegetables, citrus, cotton, potatoes)
DDT	crop insecticide (cotton)
Dieldrin	crop insecticide (cotton, corn)
Endrin	crop insecticide (cotton, grains)
Heptachlor	insecticide (termites and soil insects)
Hexa-chlorobenzene	fungicide for seed treatment
Mirex	insecticide (termites, fire ants)
Toxaphene	insecticide (livestock and crops)
PCBs	industrial chemical (heat exchange fluid for electrical transformers, paint and plastic additive)
Dioxins	unintentionally produced during combustion
Furans	unintentionally produced during combustion

ENVIRONMENTAL DEGRADATION

Hydrolysis with water:

Water reacts with the functional groups;

makes the organic part: more soluble in water,

hence more amenable to degradation by microorganisms

Reaction on mineral surfaces: Many organics bind to the surfaces of minerals in sediments

May catalyse the decomposition of substituted organics

For example, sedimentary clay minerals catalyze the hydrolysis of some chloroorganics.

Photolysis: mainly with volatile organic compounds,

Direct photolysis,

By the radicals produced by the photolysis of other atmospheric gases.

Oxidation by molecular oxygen: Unsaturated compounds are usually the most susceptible to oxidation by molecular oxygen (singlet excited state)

Microbial degradation

MICROBIAL DEGRADATION OF ORGANICS

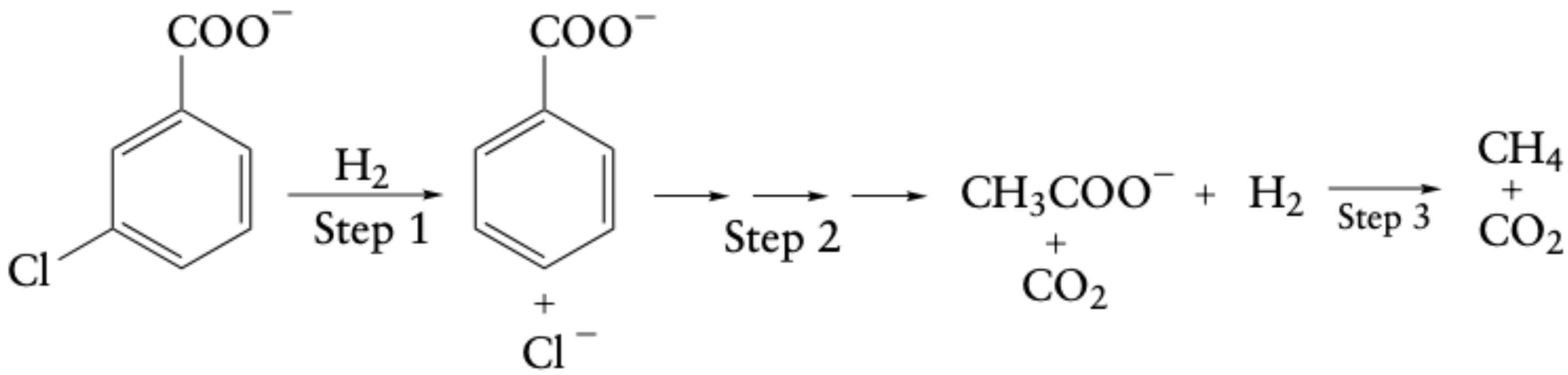
Xenobiotics

Microorganisms mutate rapidly,
so in some cases there is a mutant that can live by metabolizing the xenobiotic

usually carried out by a cooperating group of microorganisms: consortium
Different steps in the degradation are carried out by different microorganisms

Degradation of 3-chlorobenzoate

performed by three different groups of bacteria



The hydrogen generated in step 2 is utilized by the group of microorganisms doing the reductive dehalogenation in step 1

Biodegradation may result in the intermediate conversion of the carbon to new microorganisms, not achieving mineralization until these intermediate products die

The realistic goal of biodegradation is the conversion of a xenobiotic compound to a biotic one

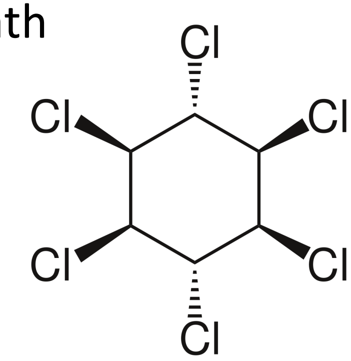
Both anaerobes and aerobes degrade xenobiotics.

Anaerobes often use reductive processes to degrade organics

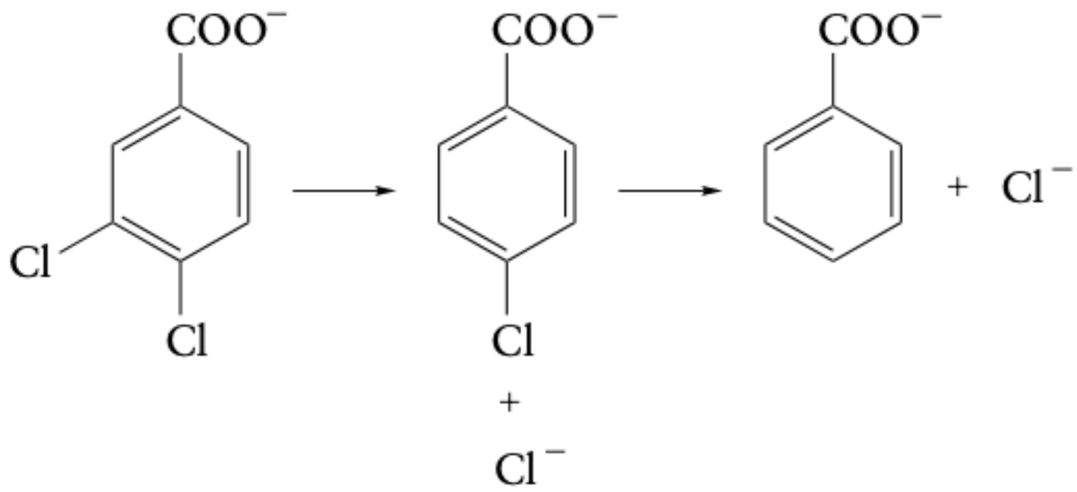
Aerobes use oxidative processes

Reductive Degradation

❖ Anaerobic dehalogenation of a pesticide was discovered during an investigation of the loss of potency of γ-hexachlorocyclohexane (Lindane) in a cattle tick bath



Principal pathway for the reductive dechlorination of 2,3-dichlorobenzoate

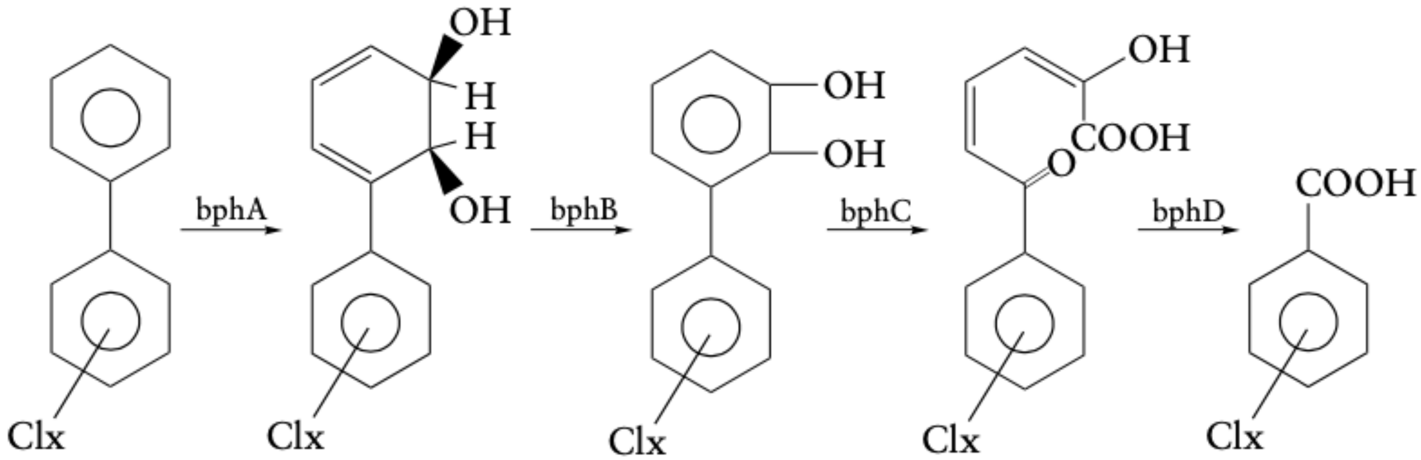


Pentachlorophenol (PCP) is rapidly converted to tetrachlorophenols,

but the subsequent loss of chloride proceeds much more slowly

Polychlorinated biphenyls (PCBs)

members of the genus Pseudomonas, degrade PCBs in the presence of oxygen



The metabolic pathways used by these diverse microorganisms for PCB destruction are similar

Aliphatic compounds

The reductive dehalogenation of aliphatic compounds has also been observed

For example, 1,1,1-trichloroethane (methylchloroform) can be reduced to the corresponding dichloro derivative

$$(Cl)_3CCH_3 + H^+ + 2e^- \longrightarrow (Cl)_2CHCH_3 + Cl^-$$

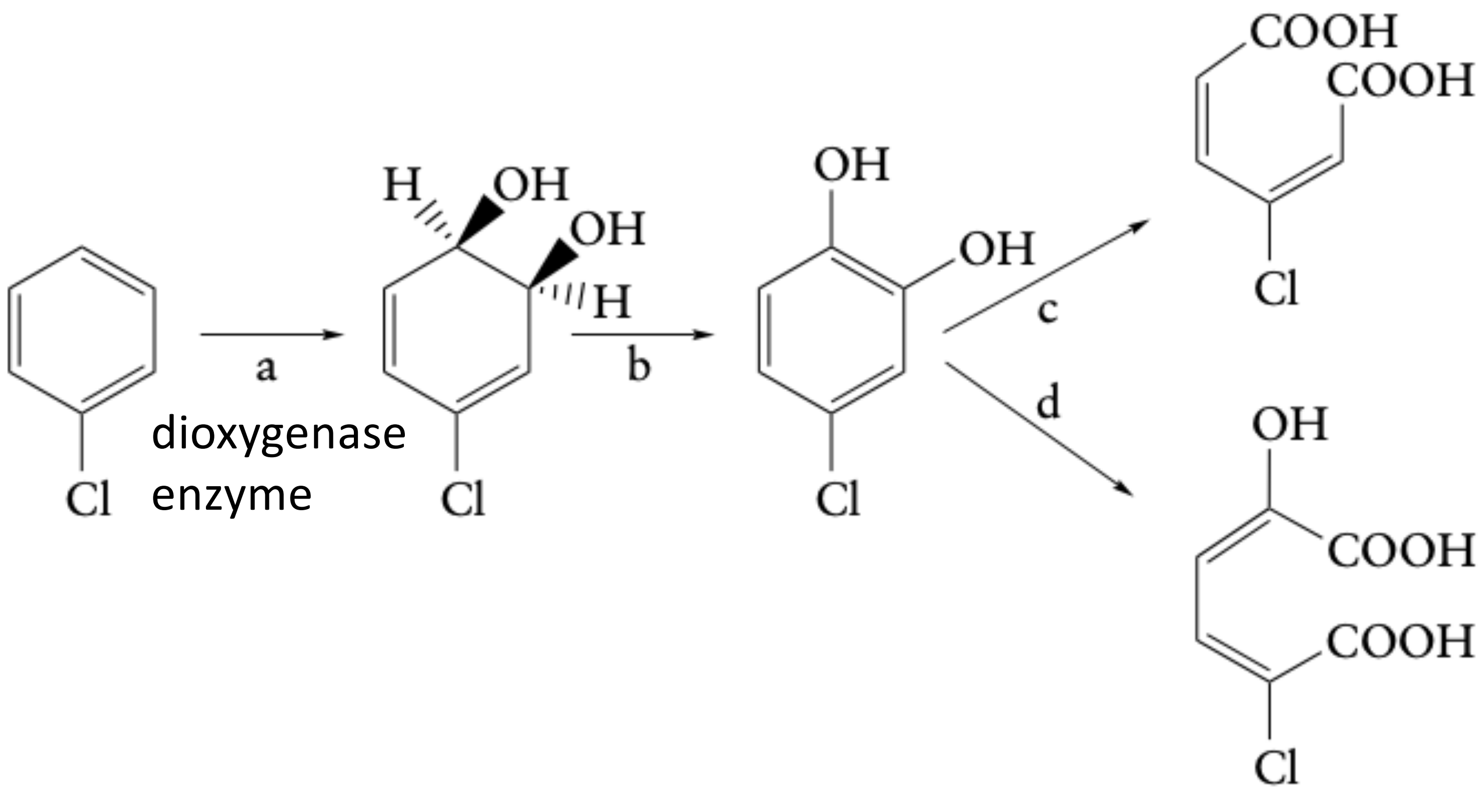
Anaerobic microorganisms reduce the chloro groups from the highly substituted biphenyls to give lightly chlorinated biphenyls, and the aerobic microorganisms destroy the lightly substituted biphenyls

Oxidative Degradation

Occur mainly with lightly chlorinated chloroorganics

because they require the attack of an electrophilic oxygen on an electron-rich center
Such as an aromatic ring or a double bond

The delocalization of these electrons by electronegative chlorine atoms decreases the electron density on the aromatic ring;
hence these compounds are less readily oxidized by molecular oxygen



readily degraded to simpler compounds and eventually to CO_2, H_2O, and Cl^-

Hydrolytic Degradation

Hydrolytic cleavage of halogens, esters, amides, and other groupings are catalyzed by both aerobes and anaerobes

$$
\begin{array}{l}
G\text{-}SH + CH_2Cl_2 \longrightarrow \underset{\substack{+ \\ HCl}}{G\text{-}SCH_2Cl} \longrightarrow \underset{\substack{+ \\ Cl^-}}{{}^{+}G\text{-}S{=}CH_2} \xrightarrow{H_2O} G\text{-}SH + CH_2O + H^+
\end{array}
$$

Glutathione (G-SH)

microorganisms that catalyse this reaction utilize formaldehyde as an energy source.

TOXICITY

- ❖ Acute or immediate toxicity to humans and animals is not usually a problem for most commercial haloorganic compounds.

- ❖ The toxicity associated with some haloorganics is of the chronic type, where the deleterious effect appears 2-30 years after the initial exposure

- ➢ For example, vinyl chloride evidently caused cancer (Liver tumour) in factory worker twenty years after they started working with it

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Most commercial halocarbons are nonpolar : removed from the bloodstream by the liver
-enzyme cytochrome P-450 (responsible for oxidative degradation of non-polar organic)

Heavily chlorinated compound : high oxidation potentials :oxidized slowly, or not at all

- ➢ high levels of this enzyme : catalyze the oxidation of other nonpolar organics such as steroids
  can change the normal hormonal balance
  can cause endocrine, immune, and neurological effects

❖ Decline in the number of eagles and hawks in the 1960s and 1970s

that correlated with the buildup of chloroorganics in the environment

Resurgence of the birds in the 1980s following the ban of the use of DDT in 1972

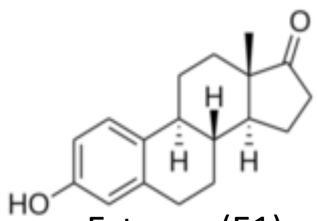
❖ Abnormal sexual development: higher levels of chloroorganics in the same animals

some industrial chemicals have hormonal activity that mimics or inhibits the activities of the sex hormones

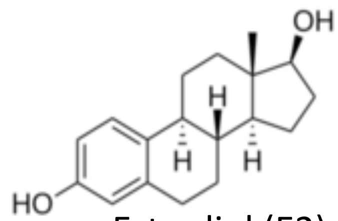
- feminization of seagulls was attributed to the higher levels of chloroorganics in these birds
- Polychlorinated bi- phenyls (PCBs) demonstrate estrogen-like activity in turtles

Estrogen, a mixture of three steroid hormones,

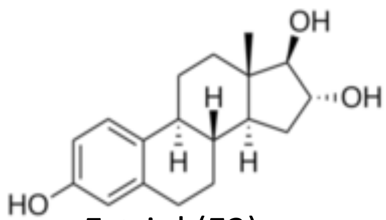
A specific ratio of estrogen to androgen (male hormones) is required during prenatal and postnatal development for sex differentiation and for the development of reproductive organs.



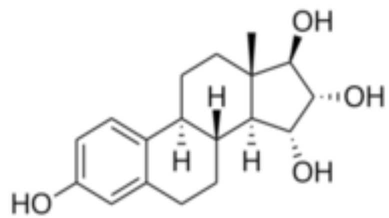
Estrone (E1)



Estradiol (E2)



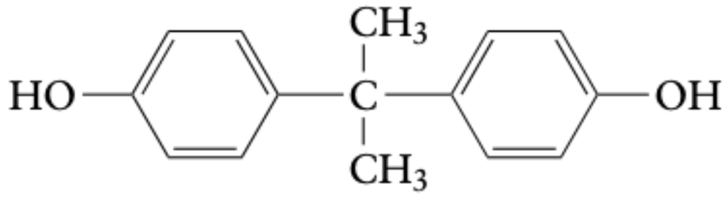
Estriol (E3)



Estetrol (E4)

produced only during pregnancy

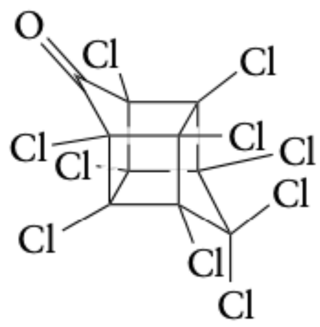
- the increases in breast cancer
- 40% decline in sperm counts in men
- increase in testicular cancer



Bisphenol A

Proposed Hormonal Activity of Environmental Compounds

Estrogen-like	Antiestrogens	Antiandrogen
PCBs	2,3,7,8-Tetrachlorodioxin	DDE
o,p-DDT	Polychlorinated benzofurans	
Methoxychlor	Benzo(*a*)pyrene	
Kepone		
Toxaphene		
Dieldrin		
Endosulfan		
Atrazine		
Bisphenol A		
Nonylphenol		



Kepone

❖ more data are required before conclusive statements can be made

❖ The toxicity associated with some haloorganics is of the chronic type, where the deleterious effect appears 2-30 years after the initial exposure

The United Nations sponsored and adopted a treaty in 2000 intended to end the production of these and other persistent chlorinated compounds throughout the world and to destroy their stocks

The ``dirty dozen'' compounds include

- the insecticides aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, and toxaphene plus
- the industrially used polychlorinated biphenyls and
- the industrial by-products, dioxins and benzo-furans

❖ The use of DDT for the control of malaria is the one exception to the ban, since the insecticide is still used for this purpose in Africa, Asia, and South America