

Lecture 11 Notes: Abiotic Chemical Transformations (Chapter 2)

Wastewater Lagoons

- Some industrial sites and mining operations may have one or more associated wastewater lagoons receiving discharges too toxic for most living organisms.
- However, there are many instances in which “spontaneous” chemical reactions occurring in such lagoons can significantly reduce the levels of toxicity before final processing and release into the environment.
- This approach works quite well provided the lagoon is not inclined to overflow during heavy rains or otherwise uncontrollably leak its contents into the nearby stream, underlying groundwater, or bay of some other neighboring body of water.
- Of course, these same chemical processes (some of which are described in the following notes) also provide sinks for the same chemical agents when they are present as environmental pollutants.

Direct Photolysis

- Light can be described in terms of both waves and particles (photons).
- Light leads to photodegradation-(photolysis) either directly or indirectly.
- Light is characterized by its wavelength distribution. Some wavelengths of light are more strongly absorbed by chemicals in the atmosphere than others (see figure 2-30), the effective cutoff for light reaching the surface of the earth is . 290 microns in wavelength.
- Treatment of light as a wave;

$\nu = c/\lambda$ where ν is the frequency in sec⁻¹ also called hertz, c is the velocity of light and λ is the wavelength in meters.

- The energy of a photon is given by: $E = h\nu = hc/\lambda$, where h is Planck’s constant, ν the frequency of the photon, c the velocity of light, and λ the photon’s wavelength.
- When considering photochemical processes, it is often more convenient to think in terms of the energy associated with “a mole of photons” (*i.e.* “einsteins”):

$$E \times N_A = 1.196 \times 10^5 / \lambda \text{ \{nm\}}$$

$$E = \text{kJ/einstein}$$

Wavelength (nm)	Energy (kJ/einstein)	Comments
290	413	Limit of UV-B at sea level
320	374	Limit of UV-A region
400	299	Violet limit of visible
750	160	Red limit of visible

Light Distribution in Water

- Affected by wavelength composition.
- Affected by light intensity (photon number/unit surface area-time).
- Angle of incidence of light entering the water.
- Optical properties of the water.
 - I = intensity, I decreases with increasing water depth due to absorbance of light by the water itself.
 - I decreases dependent on increasing concentrations of dissolved substances in water as well as with the total suspended solids (TSS) or turbidity of water.

Modeling of light intensity is done using Beers Law

Absorbance = C*Chemical molar absorptivity*path length generalizing to a broad spectrum of absorbance's due to many absorptive chemicals in water we get;

$I = I_0 e^{-\eta z}$ where z is the water depth and η (eta) is the empirical extinction coefficient [1/L]

So given the extinction coefficient we can determine the light intensity at any depth z, given the initial light intensity—light intensity can be measured by einsteins/ unit area-time or power per unit area (watts/meter squared).

- The flux of photons with wavelengths < 290 nm reaching the Earth's surface is small and consequently, direct photolysis is less important in surface waters than in the atmosphere: 290 nm \Rightarrow 413 kJ/einstein = 99 kcal/mol (average C-H bond energy).
- While photolysis within the sediment is clearly unimportant, the extent to which adsorption of chemical agents on environmental surfaces may promote (or inhibit) photolysis largely remains to be explored – the variation in surfaces being very great.
- Degradation of pentachlorophenol (a broad spectrum biocide widely used to preserve wood) is one example where direct photolysis is known to be rate-limiting in surface water at alkaline pH ($t_{1/2} = 0.86$ hr); but notice that this step and all the subsequent ones require the participation of water as a reactant.

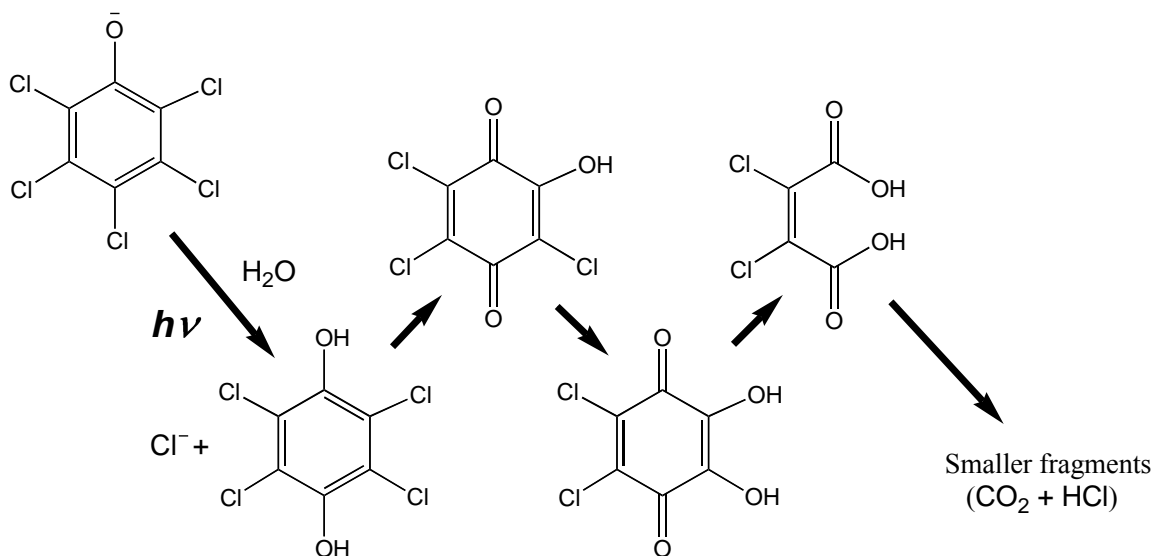


Figure 8.1 Plausible pathway for direct photolysis of the pentachlorophenolate anion.

Indirect Photodegradation

- Production of hydroxyl radical (HO^\bullet) in surface water is thought to proceed primarily through photolysis of nitrate (NO_3^-) and nitrite (NO_2^-) anions.
- The hydroxyl radical tends to either abstract a hydrogen from alkyl chains, or add to a multiple bond – the products of both these processes themselves being radicals that go on to further degradation through a cascade of reactions.
- HO^\bullet is so reactive that its involvement in any given reaction is usually inferred from product analysis; however, its low specificity is very useful in applications such as oxidative treatment of drinking water.

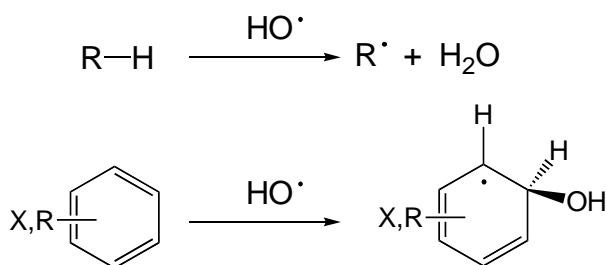
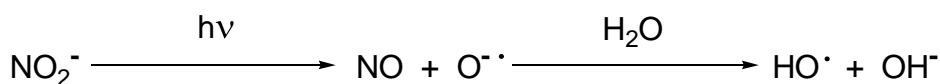
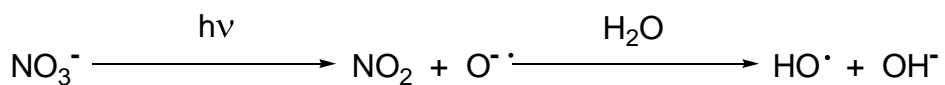


Figure 8.2 Production and Fate of Hydroxyl Radicals.

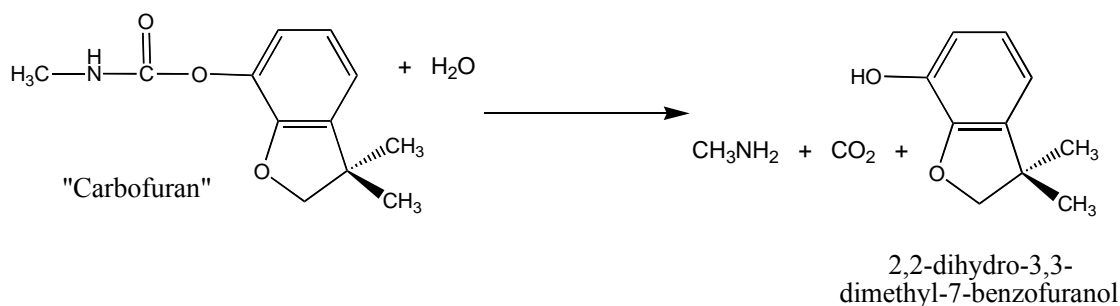
- Singlet oxygen ($^1\text{O}_2$) is another photooxidant species formed in surface waters (much more selective than the hydroxyl radical) that tends to add across multiple double bonds, or attack easily oxidized moieties like anilines, phenols, or sulfides.
- $^1\text{O}_2$ is formed from normal (triplet) oxygen ($^3\text{O}_2$) by photosensitization involving unknown chromophores probably derived from humic/fulvic acids:



Hydrolytic Processes

- Reactions with some other nucleophiles like HS^- are sometimes encountered, but the majority of environmental nucleophilic degradation pathways involve hydrolysis (*i.e.* cleavage of water).
- The important reactions are of the ester-hydrolysis type, many modern insecticides (like “Carbofuran” and “Parathion”) are of this type so that they will be relatively short lived in the environment.
- The kinetics of these processes can be expected to be pseudo-first order as the water concentration is constant; if acid- or base-catalyzed, the kinetics will be first-order in $[\text{H}^+]$ and $[\text{OH}^-]$ respectively.
- Notice that the resulting kinetics will likely be governed by some net first-order rate constant even if there are multiple nucleophilic reactions and other photolytic or redox processes involved in the degradation pathway(s).

Carbamate hydrolysis



Thiophosphate ester hydrolysis

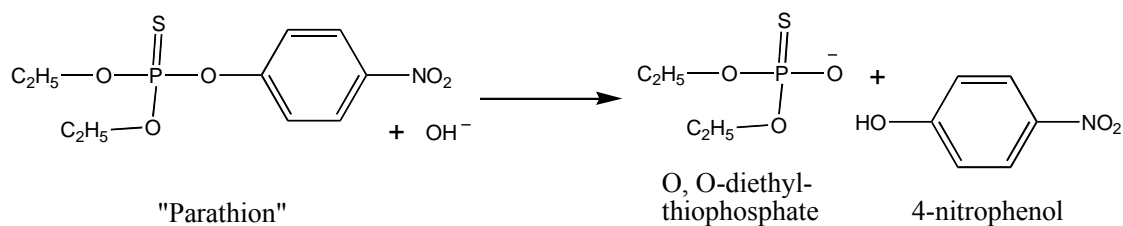


Figure 8.3 Examples of the hydrolysis of “ester-like” insecticides.

Redox Processes

- Note that hydrolysis reactions of haloalkanes are, with very few exceptions, slow reactions typically exhibiting half lives of decades to centuries under environmental conditions (!) – they are unimportant in the present context.
- Reactions such as reductive dechlorination and other abiotic redox processes are probably of much broader significance in surface waters.

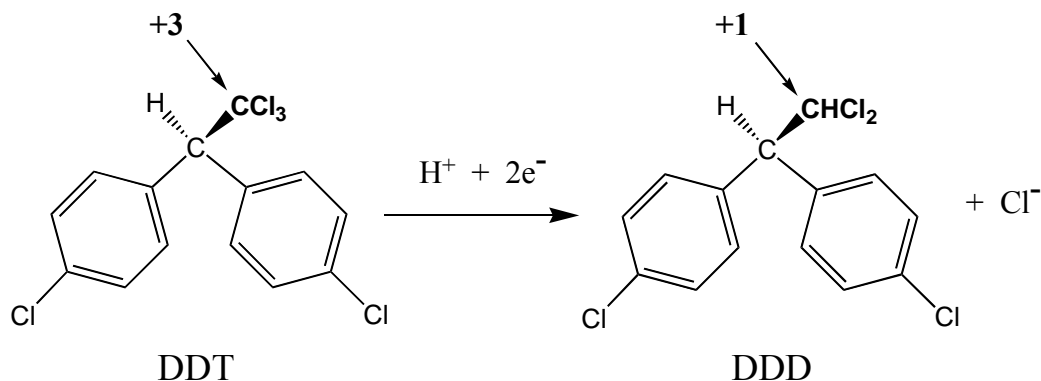


Figure 8.4 Reductive dechlorination of “dichlorodiphenyltrichloroethane.”

Next Time: Midterm Examination

Free Radicals-Definition

Free Radicals and Reactive Oxygen

A radical (often, but unnecessarily called a free radical) is an atom or group of atoms that have one or more unpaired electrons. Radicals can have positive, negative or neutral charge. They are formed as necessary intermediates in a variety of normal biochemical reactions, but when generated in excess or not appropriately controlled, radicals can wreak havoc on a broad range of macromolecules. A prominent feature of radicals is that they have extremely high chemical reactivity, which explains not only their normal biological activities, but how they inflict damage on cells.

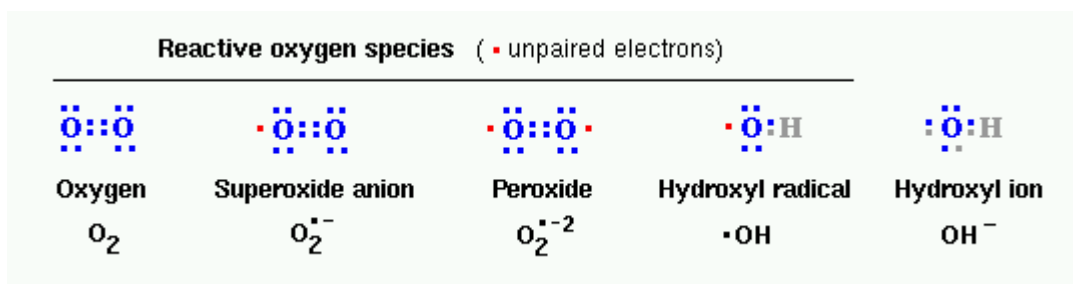
Oxygen Radicals

There are many types of radicals, but those of most concern in biological systems are derived from oxygen, and known collectively as *reactive oxygen species*. Oxygen has two unpaired electrons in separate orbitals in its outer shell. This electronic structure makes oxygen especially susceptible to radical formation.

Sequential reduction of molecular oxygen (equivalent to sequential addition of electrons) leads to formation of a group of reactive oxygen species:

- **superoxide anion**
- **peroxide** (hydrogen peroxide)
- **hydroxyl radical**

The structure of these radicals is shown in the figure below, along with the notation used to denote them. Note the difference between hydroxyl radical and hydroxyl ion, which is not a radical.



Another radical derived from oxygen is **singlet oxygen**, designated as ¹O₂. This is an excited form of oxygen in which one of the electrons jumps to a superior orbital following absorption of energy.