Photochemical reactions

Light (photon)/matter interactions

- Photon/matter interactions play roles in
 - Transformations in
 - the atmosphere
 - surface water
 - water & wastewater treatment (e.g., disinfection, engineered wetland)
 - Analysis
 - Light absorption $f(\lambda, C_{compound})$ determine $C_{compound}$ by a spectrophotometer
- Photolytic transformations are often non-specific
 - Attack bonds & structures resistant to biodegradation & other pathways
 - Can be applicable to synthetic chemicals
 - Potential for complete mineralization CO_2 , H_2O , inorganic N & P
 - Combine with photocatalysts visible light catalysis

Light (photon)/matter interactions

- Light interact with matter in two ways
 - (1) Scattering
 - Elastic process (energy of light not substantially changed)

(2) Absorption

- Capture of the photon
- Moves electron from low energy (ground) to high energy state



Basic laws of photochemistry

- Grotthuss-Draper Law (1st law of photochemistry): Light must be absorbed in order for a photochemical reaction to take place
- Stark-Einstein Law (2nd law of photochemistry): For each photon of light absorbed by a chemical system, only one molecule is activated

Photolysis – general

Molecule + photon \longrightarrow Molecule* \longrightarrow Products

(direct photolysis)

• Photolysis

- Refers to light induced chemical transformations
- Requires absorption of a photon by a molecule

• Photon absorption

- As a consequence, electrons are excited: may break the covalent bond to produce a different compound
- Absorptivity typically wavelength & solvent dependent

Photolysis – general

• Light: source of energy

$$E = h\nu = h\frac{c}{\lambda}$$

E = energy of a photon (J/photon)

- $h = 6.626 \times 10^{-34}$ J·s, Planck constant
- ν = frequency of light (s⁻¹)
- $c = 3.0 \times 10^8$ m/s, speed of light in a vacuum
- λ = wavelength of light (m)

On a molar basis,

 $\boldsymbol{E} = 6.02 \times 10^{23} \cdot h \frac{c}{\lambda} = \frac{1.196 \times 10^5}{\lambda} kJ/einstein$

E = energy of light on a molar basis (kJ/einstein) <u>einstein: 1 mole of photons</u> λ = wavelength of light in <u>nm</u>

Solar flux & absorption



Bond energies & light absorption

Table 15.1 Typical Energies for SomeSingle Bonds and the ApproximateWavelengths of Light Corresponding toThis Energy ^a

Bond	Bond Energy <i>E^b</i> (kJ·mol ⁻¹)	Wavelength λ (nm)
O-H	465	257
HH	436	274
CH	415	288
N–H	390	307
CO	360	332
CC	348	344
CCl	339	353
ClCl	243	492
Br-Br	193	620
0–0	146	820

Compare to:

$$E = \frac{1.196 \times 10^5}{\lambda} kJ/einstein$$

Energy of UV/visible light
 ~ covalent bonds

→ The covalent bonds may be cleaved as a consequence of UV/visible light absorption

^a Compare Eq. 15-3. ^b Values from Table 2.2.

Absorbance

- Whether the photochemical reactions will take place depends on
 - i) The probability with which a given compound absorbs light of a given wavelength
 - ii) The probability that the excited species undergoes a particular reaction
- Absorbance: Beer-Lambert law

$$A(\lambda) = \log_{10} \frac{I_0(\lambda)}{I(\lambda)} = [\alpha(\lambda) + \varepsilon_i(\lambda)C_i] \cdot l$$

$$\begin{split} A &= \text{absorbance} \\ I_0 \& I &= \text{light intensity at } x=0 \& I, \text{ respectively (e.g., in einstein/cm²-s)} \\ \alpha &= \text{absorption coefficient of the solvent (cm⁻¹)} \\ \varepsilon_i &= \text{molar absorption coefficient for solute } i (M^{-1} \cdot \text{cm}^{-1}) \\ C_i &= \text{ concentration of solute } i (M) \end{split}$$

l = path length of light (cm)

Absorption spectrum

• Absorption spectrum easily measurable by UV-Vis spectrophotometer



0.1 mM nitrobenzene in aqueous solution

Chromophores & light absorption

Chromophore	λ_{max} , nm	$\epsilon @ \lambda_{max}$	Transition
C-C	<180	1000	$\sigma \rightarrow \sigma^*$
C-H	<180	1000	$\sigma \rightarrow \sigma^*$
C=C	180	10,000	$\pi \rightarrow \pi^*$
C=C-C=C	220	20000	$\pi \rightarrow \pi^*$
C=C-C=O	220	20000	$\pi \rightarrow \pi^*$
Benzene	260	200	$\pi \rightarrow \pi^*$
Phenol	275	1500	$\pi \rightarrow \pi^*$
Aniline	380	10,000	$\pi \rightarrow \pi^*$
Ar-NO2	280	7000	$\pi \rightarrow \pi^*$
Napthalene	310	200	$\pi \rightarrow \pi^*$
Anthracene	380	10,000	$\pi \rightarrow \pi^*$
Indole	290	5000	$\pi \rightarrow \pi^*$
RS-SR	300	300	$n \rightarrow \sigma^*$
C=N	<220	20	$n \rightarrow \pi *$
C=O	280	20	$n \rightarrow \pi *$
N=O	300	100	$n \rightarrow \pi *$
N=N	350	100	$n \rightarrow \pi *$
C=C-C=O	350	30	$n \rightarrow \pi *$
Benzoquinone	370	500	$n \rightarrow \pi *$
N=O	660	200	$n \rightarrow \pi *$

Chromophore

A structural moiety that exhibits a characteristic UV/Vis absorption spectrum

- Delocalized π electrons are often good chromophores
- λ<290 nm strongly absorbed in the atmosphere → not significant at natural conditions

 λ_{max} : maximum absorption wavelength ϵ : molar extinction coefficient

What happens after a molecule absorbs light?



When molecule A absorbs a photon

$$A \xrightarrow{h\nu} A^{*}$$

$$A^{*} \longrightarrow B + C$$

$$A^{*} + D \longrightarrow B + C$$

$$A^{*} + B \longrightarrow A + C + D$$

$$A^{*} + B \longrightarrow A + C + D^{*}$$

$$A^{*} + B \longrightarrow A + C + D^{*}$$

$$A^{*} + B \longrightarrow A + B^{*}$$

$$B^{*} + C \longrightarrow B + E + F$$

$$A^{*} + B^{*} \longrightarrow A + B$$

$$A^{*} + M \longrightarrow A + M$$

Direct photolysis



Figure 15.7 Examples of direct photochemical reaction pathways: (a) substituted chlorobenzenes, (b) trifluralin, and (c) a ketone (from Mill and Mabey, 1985).

Direct photolysis



Direct photolysis – transformation issues

- Often have multiple pathways after photon absorption
 - Multiple products
 - Multiple deactivation routes
 - Thermal
 - Phosphorescence/fluorescence
 - Interactions with solvent/solutes
- Quantum yield, $\boldsymbol{\Phi}(\boldsymbol{\lambda})$
 - Moles of compound transformed per moles of photons absorbed by the compound
 - Pathway specific or overall yields
 - Φ s are often <<1; $10^{-2} 10^{-6}$

Direct photolysis – transformation issues

- Quantum yield, $\boldsymbol{\Phi}(\boldsymbol{\lambda})$
 - Quantum yield for reaction pathway j

 $\Phi_{ij}(\lambda) = \frac{(number \ of \ molecules \ i \ reacting \ by \ pathway \ j)}{(total \ number \ of \ photons \ of \ wavelength \ \lambda \ absorbed}$ by the system owing to the presence of the compound \ i)

Reaction quantum yield (for all reaction pathways)

 $\Phi_{ir}(\lambda) = \frac{(total number of molecules i transformed)}{(total number of photons of wavelength \lambda absorbed by the system owing to the presence of the compound i)}$

- The reaction quantum yield has to determined by experiments

$$A(\lambda) = \log_{10} \frac{W_0(\lambda)}{W(\lambda)} = [\alpha(\lambda) + \varepsilon_i(\lambda)C_i] \cdot l$$

 $W_0(\lambda) \& W(\lambda)$ = light intensity at the water surface & at the underwater position of interest, respectively (einstein/cm²-s)

Generally the light absorption by compound *i* is much smaller than other constituents in water

$$log_{10}\frac{W_0(\lambda)}{W(\lambda)}\approx \alpha(\lambda)\cdot l$$



$$\alpha(\lambda) \cdot l = \alpha_D(\lambda) \cdot z_{mix}$$

 $\alpha_D(\lambda)$ = diffuse attenuation coefficient (cm⁻¹) $z_{mix} = V/A$ = depth of mixed water body (cm) V = volume of the water body (cm³) A = surface area of the water body (cm²)

- $l \neq z_{mix}$ because:
 - i) The sunlight is not always perpendicular to water surface
 - ii) Light is scattered by suspended particles
 - iii) Light is absorbed and then reemitted by particles and dissolved matter





so
$$W(z_{mix}, \lambda) = W_0(\lambda) \cdot 10^{-\alpha_D(\lambda) \cdot z_{mix}}$$

Define
$$D(\lambda)$$
 as: $D(\lambda) = \frac{l(\lambda)}{z_{mix}}$
 $\alpha_D(\lambda) = D(\lambda)\alpha(\lambda)$
 $D(\lambda) = distribution function$
For non-turbid water, 1.05~1.3
For very turbid water, up to 2.0

 $\alpha(\lambda)$ -- can be determined by a spectrophotometer; $D(\lambda)$ -- can be determined by database or computer programs at the region of interest

Out interest: how much light will be absorbed between the depth of 0 to z_{mix} by a pollutant (per volume basis)

1) Rate of light absorption by all species in water (per surface area; in einstein/cm²-s)

$$= W_0(\lambda) - W(z_{mix}, \lambda) = W_0(\lambda) \left[1 - 10^{-\alpha_D(\lambda) \cdot z_{mix}}\right]$$

2) Rate of light absorption by all species in water (per volume; in einstein/cm³-s)

$$=\frac{W_0(\lambda)}{z_{mix}} \left[1 - 10^{-\alpha_D(\lambda) \cdot z_{mix}}\right]$$

3) Fraction of light absorbed by a pollutant *i*:

$$F_i =$$

4) Rate of light absorption by compound *i* per volume:

$$= (system \ light \ absorption, vol. \ basis) \times F_i$$
$$= \frac{W_0(\lambda)}{z_{mix}} \left[1 - 10^{-\alpha_D(\lambda) \cdot z_{mix}}\right] \frac{\epsilon_i(\lambda)}{\alpha(\lambda)} C_i$$

Rate of light absorption by compound *i*, $I_a(\lambda)$:

$$I_{a}(\lambda) = \frac{W_{0}(\lambda) \cdot \epsilon_{i}(\lambda) \cdot \left[1 - 10^{-\alpha_{D}(\lambda) \cdot z_{mix}}\right]}{z_{mix} \cdot \alpha(\lambda)} C_{i}$$

 $= k_{a}(\lambda) \cdot C_{i}$ $I_{a}(\lambda) \text{ in einstein/L-s}$ $W_{0}(\lambda) \text{ in <u>millieinstein/cm²-s</u>}$ $\epsilon_{i}(\lambda) = \text{molar absorption coeff. for compound } i \text{ (L/mole-cm)}$ $C_{i} = \text{concentration of compound } i \text{ (mole/L)}$ $k_{a}(\lambda) = \underline{specific \ light \ absorption \ rate \ (einsten/mole-s)}$

Direct photolysis rate at specific λ

$$\begin{pmatrix} Photolysis \\ rate \end{pmatrix} = \begin{pmatrix} Light \\ absorption rate \end{pmatrix} \times \begin{pmatrix} Transformation rate \\ when light is absorbed \end{pmatrix}$$
$$- \begin{pmatrix} \frac{dC_i}{dt} \end{pmatrix}_{\lambda} \qquad I_a(\lambda) \qquad \Phi_{ir}(\lambda)$$

$$-\left(\frac{dC_i}{dt}\right)_{\lambda} = \Phi_{ir}(\lambda)I_a(\lambda) = \Phi_{ir}(\lambda)k_a(\lambda)C_i$$

The direct photolysis rate is in 1st order only if $\varepsilon_i(\lambda)C_i \ll \alpha(\lambda)$

$$-\left(\frac{dC_i}{dt}\right)_{\lambda} = k_p(\lambda)C_i$$

 $k_p(\lambda) =$ <u>the direct photolysis 1st-order rate constant at</u> wavelength λ (s⁻¹) = $\Phi_{ir}(\lambda)k_a(\lambda)$

Direct photolysis – overall rate

The overall rate of direct photolysis

$$= -\frac{dC_i}{dt} = \left[\sum_{\lambda} k_p(\lambda)\right] C_i = k_p C_i$$

k_p = <u>the overall direct photolysis 1st-order rate</u> <u>constant (s⁻¹)</u>

If Φ_{ir} is not a function of λ , then:

$$-\frac{dC_i}{dt} = \Phi_{ir} \left[\sum_{\lambda} k_a(\lambda) \right] C_i = \Phi_{ir} k_a C_i$$

k_a = <u>the overall specific light absorption rate</u> (einsten/mole-s)

Direct photolysis – natural water

- Two limiting cases:
 - Negligible light absorption (clear lake surface, z_{mix} small)
 - 2) Nearly all light absorbed (turbid water, z_{mix} large)



1) Negligible light absorption (near surface)

We approximate our solution in the case of $\alpha_D(\lambda) z_{mix} \leq 0.02$

$$-\frac{dC_{i}}{dt} = \left[\sum_{\lambda} k_{p}(\lambda)\right] C_{i} = \left[\sum_{\lambda} \Phi_{ir}(\lambda) k_{a}(\lambda)\right] C_{i}$$

$$= \left[\sum_{\lambda} \frac{\Phi_{ir}(\lambda) \cdot W_{0}(\lambda) \cdot \epsilon_{i}(\lambda) \cdot [1 - 10^{-\alpha_{D}(\lambda) \cdot z_{mix}}]}{z_{mix} \cdot \alpha(\lambda)}\right] C_{i}$$

$$\frac{1 - 10^{-\alpha_{D}(\lambda) \cdot z_{mix}} \approx 2.303 \alpha_{D}(\lambda) \cdot z_{mix}}{(when \alpha_{D}(\lambda) z_{mix} \leq 0.02)}$$

$$= 2.303 \left[\sum_{\lambda} \frac{\Phi_{ir}(\lambda) \cdot W_{0}(\lambda) \cdot \epsilon_{i}(\lambda) \cdot \alpha_{D}^{0}(\lambda)}{\alpha(\lambda)}\right] C_{i}$$

$$\frac{\text{Define}}{Z(\lambda) = \frac{W_{0}(\lambda) \cdot \alpha_{D}^{0}(\lambda)}{\alpha(\lambda)} = W_{0}(\lambda) \cdot D^{0}(\lambda)$$

$$(Z(\lambda) \text{ has a unit of millieinstein/cm2/s)}$$

$$= 2.303 \left[\sum_{\lambda} Z(\lambda) \cdot \epsilon_{i}(\lambda) \cdot \Phi_{ir}(\lambda)\right] C_{i}$$

$$26$$

1) Negligible light absorption (near surface)

So, in the case of $\alpha_D(\lambda) z_{mix} \leq 0.02$, the direct photolysis rate is given as:

$$-\frac{dC_i}{dt} = 2.303 \left[\sum_{\lambda} Z(\lambda) \cdot \epsilon_i(\lambda) \cdot \Phi_{ir}(\lambda) \right] C_i = k_p^0 C_i$$

 k_p^{0} = near surface photolysis rate (s⁻¹)

If Φ_{ir} is not a function of λ , then:

$$-\frac{dC_i}{dt} = 2.303 \left[\sum_{\lambda} Z(\lambda) \cdot \epsilon_i(\lambda) \right] \Phi_{ir} C_i = k_a^{0} \Phi_{ir} C_i$$

 k_a^0 = near surface specific light absorption rate (einsten/mole-s)

Realistic example – k_a^0

Q: Calculate k_a^{0} of para-nitroacetophenone (PNAP) at 40°N altitude at noon on a clear midsummer day.



 $W(noon, \lambda)$ is obtained from database or computer program

 $Z(noon, \lambda) = W(noon, \lambda) \cdot D^{0}(\lambda),$ D⁰(\lambda) is obtained from database or computer program

		$W(\text{noon},\lambda)^{b,d}$	$Z(\text{noon},\lambda)^{b,d}$
λ (Center) (nm)	$\lambda \operatorname{Range}(\Delta \lambda)$ (nm)	(millieinstei	n · cm ⁻² s ⁻¹)
297.5	2.5	1.08(-9)	1.19(-9)
300.0	2.5	3.64(-9)	3.99(-9)
302.5	2.5	1.10(-8)	1.21(-8)
305.0	2.5	2.71(-8)	3.01(-8)
307.5	2.5	4.55(-8)	5.06(-8)
310.0	2.5	7.38(8)	8.23(-8)
312.5	2.5	1.07(-7)	1.19(7)
315.0	2.5	1.43(-7)	1.60(-7)
317.5	2.5	1.71(7)	1.91(-7)
320.0	2.5	2.01(-7)	2.24(-7)
323.1	3.75	3.75(-7)	4.18(-7)
330.0	10	1.27(-6)	1.41(-6)
340.0	10	1.45(6)	1.60(-6)
350.0	10	1.56(6)	1.71(-6)
360.0	10	1.66(-6)	1.83(-6)
370.0	10	1.86(-6)	2.03(-6)
380.0	10	2.06(6)	2.24(-6)
390.0	10	2.46(6)	2.68(-6)
400.0	10	3.52(-6)	3.84(-6)
420.0	30	1.40(-5)	1.51(-5)
450.0	30	1.77(-5)	1.90(-5)
480.0	30	1.91(-5)	2.04(-5)
510.0	30	1.99(-5)	2.12(-5)
540.0	30	2.10(-5)	2.22(-5)
570.0	30	2.13(-5)	2.25(5)
600.0	30	2.13(-5)	2.24(-5)
640.0	50	3.54(-5)	3.72(-5)

Realistic example – k_a^0



Realistic example – k_a^0

	Solar Ir	radiance	PNAP		
λ (Center) (nm)	λRange (Δλ) (nm)	$Z(\text{noon},\lambda)^a$ (millieinstein \cdot cm ⁻² s ⁻¹)	$\varepsilon_i(\lambda)^{b}$ (cm ⁻¹ M ⁻¹)	$k_{a}^{0}(\lambda) = 2.3 Z(\lambda)\varepsilon_{i}(\lambda)$ [einstein (mol PNAP) ⁻¹ s ⁻¹] 10 ³ k_{a}^{0}(\lambda)	
297.5	2.5	1.19(9)	3790	0.01	
300.0	2.5	3.99(-9)	3380	0.03	
302.5	2.5	1.21(-8)	3070	0.09	
305.0	2.5	3.01(-8)	2810	0.20	
307.5	2.5	5.06(-8)	2590	0.30	
310.0	2.5	8.23(-8)	2380	0.45	
312.5	2.5	1.19(-7)	2180	0.60	
315.0	2.5	1.60(-7)	1980	0.73	
317.5	2.5	1.91(-7)	1790	0.79	
320.0	2.5	2.24(-7)	1610	0.83	
323.1	3.75	4.18(-7)	1380	1.33	
330.0	10	1.41(-6)	959	3.12	
340.0	10	1.60(6)	561	2.06	
350.0	10	1.71(-6)	357	1.42	
360.0	10	1.83(6)	230	0.97	
370.0	10	2.03(-6)	140	0.66	
380.0	10	2.24(6)	81	0.41	
390.0	10	2.68(-6)	45	0.28	
400.0	10	3.84(-6)	23	0.22	
420.0	30	1.51(-5)	0	0	
450.0	30	1.90(-5)	0	0	
				$k_a^0 = \Sigma k_a^0(\lambda) = 14.5 \cdot 10^{-3}$ einstein (mol·PNAP) ⁻¹ s ⁻¹	

2) Nearly all light absorbed

We approximate our solution in the case of $\alpha_D(\lambda) z_{mix} \ge 2$

$$-\frac{dC_{i}}{dt} = \left[\sum_{\lambda} \frac{\Phi_{ir}(\lambda)W_{0}(\lambda) \cdot \epsilon_{i}(\lambda) \cdot \left[1 - 10^{-\alpha_{D}(\lambda) \cdot z_{mix}}\right]}{z_{mix} \cdot \alpha(\lambda)}\right]C_{i}$$

$$1 - 10^{-\alpha_{D}(\lambda) \cdot z_{mix}} \approx 1$$
(when $\alpha_{D}(\lambda)z_{mix} \ge 2$)

$$-\frac{dC_i}{dt} = \left[\sum \frac{W_0(\lambda) \cdot \epsilon_i(\lambda) \cdot \Phi_{ir}(\lambda)}{\alpha(\lambda) z_{mix}}\right] C_i = k_p^{\ t} C_i$$

 k_p^{t} = photolysis rate of optically thick zone(s⁻¹)

Direct photolysis – natural water

Q: Estimate the 24 h averaged direct photolysis half-life of 4-nitrophenol (4NP) near the surface of a lake (pH=7.5). Following 24-h averaged near-surface total specific light absorption rates have been determined for non-dissociated (HA) and dissociated (A^{-}) species (pK_a = 7.11):

$$k_a^{0}(HA) = 4.5 \times 10^{3} \text{ einstein} \cdot (\text{mole } HA)^{-1} \cdot d^{-1}$$

$$k_a^{0}(A^{-}) = 3.2 \times 10^4 \ einstein \cdot (mole \ A^{-})^{-1} \cdot d^{-1}$$

The quantum yields for the two species are as follows (assume the quantum yields are identical for all wavelengths):

```
\Phi_{ir}(HA) = 1.1 \times 10^{-4} (mole HA) \cdot einstein^{-1}\Phi_{ir}(A^{-}) = 8.1 \times 10^{-6} (mole A^{-}) \cdot einstein^{-1}
```

Indirect (sensitized) photolysis



- UC: Unknown chromophore ex) colored DOM (CDOM)
- Singlet oxygen (¹O₂): excited state
- Triplet oxygen (³O₂): ground state
- Photochemically-produced reactive intermediates (PPRIs)

Figure 16.2 Pathways for indirect photolysis of an organic compound *i* involving excited natural organic matter constituents. UC refers to unknown chromophores. Wavy arrows symbolize radiationless transition (adapted from Zafiriou et al., 1984).

PPRIs

Products		Possible production processes
Singlet Oxygen	$^{1}O_{2}$	Sensitized by excited DOM
Superoxide anion	O_2^{-}	Photolysis of Fe(III) complexes; deprotonation of HO_2 .
Hydroperoxyl radical	HO_2	Uptake from atmosphere, protonation of O_2^{-}
Hydrogen Peroxide	H_2O_2	Photolysis of Fe(III) complexes; disproportionation of superoxide anion
Ozone	O_3	Uptake from atmosphere
Hydroxyl radical	$\cdot OH$	Photolysis of Fe(III) complexes, H_2O_2 , NO_3^- , NO_2^- ; decomposition of O_3
Organic peroxy radicals	ROO.	Photolysis of DOM
Aquated electron	eaq	Photolysis of DOM

Adapted from Stumm and Morgan (1996)

Steady-state concentrations of PPRIs



Figure 16.1 Ranges of steady-state concentrations of reactive oxygen species in sunlit surface waters (sw), sunlit cloud waters (cw), drinking-water treatment (dw), and the troposphere (trop(g)). Data from Sulzberger et al. (1997) and Atkinson et al. (1999).

ex) $[{}^{1}O_{2}]_{ss} \sim 10^{-13} \text{ M}$ (summer, noon) $k_{phenol} \sim 10^{7} \text{ M}^{-1} \text{s}^{-1}$ $k_{phenolate} \sim 10^{8} \text{ M}^{-1} \text{s}^{-1}$ $pK_{a} \sim 10$ $t_{1/2}$, phenol_T = ?

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Reactions with hydroxyl radical



- Especially important for advanced oxidation processes
- Major reaction pathways:
 - Electrophilic addition to a double bond or aromatic ring
 - Abstraction of a hydrogen atom from a carbon atom

Figure 16.3 Second-order rate constants for reaction with HO[•] in aqueous solution ($k_{p,HO}$; Eq. 16-7) for a series of organic compounds. Data from http://allen.rad.nd.edu, and Haag and Yao (1992).