Photochemical reactions III: Indirect photolyis

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		Potential production processes
Singlet oxygen	$^{1}O_{2}$	Sensitized by excited DOM
Superoxide anion	O ₂ -•	Photolysis of Fe(III) complexes; deprotonation of HO_2^{\bullet}
Hydroperoxyl radical	HO ₂ •	Uptake from atmosphere, protonation of $O_2^{-\bullet}$
Hydrogen peroxide	H ₂ O ₂	Photolysis of Fe(III) complexes; disproportionation of superoxide anion
Ozone	O ₃	Uptake from atmosphere
Hydroxyl radical	•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	e- _{eq}	Photolysis of DOM

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).

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
 - * Diffusion controlled reaction: reaction occurs readily when collision occurs

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

Photochemical reactions IV: Exercise

Direct photolysis: For cmpd with 2 species

Q: Estimate the 24 h averaged direct photolysis half-life of 4nitrophenol (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):

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

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

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

$$\Phi_{ir}(HA) = 1.1 \times 10^{-4} (mole HA) \cdot einstein^{-1}$$

$$\Phi_{ir}(A^{-}) = 8.1 \times 10^{-6} (mole A^{-}) \cdot einstein^{-1}$$

Solution)

Here 4NP exists in the water in either non-dissociated (HA) or dissociated (A^-) form, and the half-life is to be estimated for the sum of [HA] and [A^-]:

$$[HA]_{total} = [HA] + [A^{-}]$$
(1)

Denote $k_p^{0}(HA_{total})$ as the 1st order photolysis rate for the sum of HA and A⁻:

$$-\frac{d[HA]_{total}}{dt} = k_p^{0}(HA_{total}) \times [HA]_{total}$$
(2)

Then:

$$-\frac{d[HA]_{total}}{dt} = -\left(\frac{d[HA]}{dt} + \frac{d[A^{-}]}{dt}\right) = -\left\{k_p^{0}(HA) \times [HA] + k_p^{0}(A^{-}) \times [A^{-}]\right\}$$
(3)

From (1)-(3):

$$k_p^{0}(HA_{total}) = \alpha_{ia} \times k_p^{0}(HA) + (1 - \alpha_{ia})k_p^{0}(A^{-})$$

where
$$\alpha_{ia} = \frac{[HA]}{[HA]_{total}}$$

Now, recall from acid-base equilibrium:

$$HA = H^+ + A^-$$

 $K_a = \frac{[H^+][A^-]}{[HA]} = 10^{-7.11}$

Therefore,

$$\alpha_{ia} = \frac{[HA]}{[HA]_{total}} = \frac{[HA]}{[HA] + [A^-]} = \frac{[HA]}{[HA] + K_a [HA]/[H^+]} = \frac{1}{1 + K_a/[H^+]}$$
$$= \frac{1}{1 + 10^{-7.11}/10^{-7.5}} = 0.289$$

Get photolysis rate constants for each species:

$$k_p^{0}(HA) = \Phi_{ir}(HA) \times k_a^{0}(HA) = (4.5 \times 10^3) \times (1.1 \times 10^{-4}) = 0.495 \ d^{-1}$$
$$k_p^{0}(A^{-}) = \Phi_{ir}(A^{-}) \times k_a^{0}(A^{-}) = (3.2 \times 10^4) \times (8.1 \times 10^{-6}) = 0.259 \ d^{-1}$$

*Now we are ready to get the photolysis rate constant for HA*_{total}*:*

$$k_p^{0}(HA_{total}) = \alpha_{ia} \times k_p^{0}(HA) + (1 - \alpha_{ia})k_p^{0}(A^{-})$$

= 0.289 × 0.495 d⁻¹ + (1 - 0.289) × 0.259 d⁻¹ = 0.327 d⁻¹

Half-life is defined for a 1st-order reaction as:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{0.327 \ d^{-1}} = 2.1 \ days$$

We see half-life for 4NP should depend on pH.

Direct photolysis: For multiple wavelengths

Q: Following data are obtained for a clear midsummer day (averaged over 24 hours) and nitrobenzene. Using a reaction quantum yield of 2.9×10^{-3} for all wavelengths, determine the photolysis half-life of nitrobenzene in a well-mixed water body with negligible light absorption if clear days continue in the middle of summer.

Wavelength range (cm)	Center of wavelength (cm)	Z(24 h <i>,</i> λ) (millieinstein/cm²-d)	Molar absorption coeff. (M ⁻¹ cm ⁻¹)
315-325	320	0.0073	800
325-335	330	0.0137	580
335-345	340	0.0187	560
345-355	350	0.0216	280

Solution)

For negligible light absorption with a wavelength-invariant Φ_{ir} , the near surface photolysis rate is given by:

$$k_p^{\ 0} = k_a^{\ 0} \Phi_{ir} = 2.303 \left[\sum_{\lambda} Z(\lambda) \cdot \varepsilon_i(\lambda) \right] \Phi_{ir}$$

Center of wavelength (cm)	Z(24 h, λ) (millieinstein/cm²-d)	Molar absorption coeff. (ε _i (λ); M ⁻¹ cm ⁻¹)	Ζ(24 h, λ) × ε _i (λ)
320	0.0073	800	5.84
330	0.0137	580	10.47
340	0.0187	560	6.05
350	0.0216	280	30.31
		Sum	30.31

Unit for Z(24 h, λ) × $\varepsilon_i(\lambda)$:

millieinstein/cm²-d × L/mol-cm × 10⁻³ einsten/millieinstein × 10³ cm³/L

= einstein/mol-d

$$k_p^{0} = 2.303 \left[\sum_{\lambda} Z(\lambda) \cdot \varepsilon_i(\lambda) \right] \Phi_{ir}$$

= 2.303 × (30.31 einstein/mol – d) × (2.9 × 10⁻³ mol/einstein)
= 0.202 d⁻¹

$$t_{1/2} = \frac{\ln 2}{k_p^0} = \frac{\ln 2}{0.202 \ d^{-1}} = \mathbf{3.43} \ \mathbf{d}$$

Indirect photolysis: For cmpd with 2 species

Q: Phenol was accidently released to a well-mixed pond with a pH of 7.0. How long will it take for the total phenol concentration $([\text{phenol}_T] = [C_6H_5OH] + [C_6H_5O^-])$ to be reduced into half by indirect photolysis with singlet oxygen (¹O₂) as a PPRI? Assume a steady-state singlet oxygen concentration of 10⁻¹³ M in the pond. The second order rate constants for phenol (C₆H₅OH) and phenolate (C₆H₅O⁻) with singlet oxygen are 10⁷ M⁻¹s⁻¹ and 10⁸ M⁻¹s⁻¹, respectively. Use the acid dissociation constant (K_a) of 10⁻¹⁰ for phenol.

* hint:
$$\frac{d[phenol_T]}{dt} = -k_{1,phenol_T}[phenol_T]$$
$$= -k_{1,C_6H_5OH}[C_6H_5OH] - k_{1,C_6H_5O}-[C_6H_5O^-]$$

where
$$k_{1,i} = k_{2,i} \begin{bmatrix} {}^{1}O_{2} \end{bmatrix}_{ss}$$
 $k_{1,i} = pseudo first order rate constant for i$
 $k_{2,i} = second order rate constant for i$

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Solution)

$$\frac{d[C_6H_5OH]}{dt} = -k_{2,C_6H_5OH} \left[{}^{1}O_2 \right]_{ss} \left[C_6H_5OH \right] = -k_{1,C_6H_5OH} \left[C_6H_5OH \right]$$

$$\frac{d[C_6H_5O^-]}{dt} = -k_{2,C_6H_5O^-} \left[{}^{1}O_2 \right]_{ss} \left[C_6H_5O^- \right] = -k_{1,C_6H_5O^-} \left[C_6H_5O^- \right]$$

$$\log \frac{[C_6 H_5 O^-]}{[C_6 H_5 OH]} = pH - pK_a = 3$$

 $\frac{k_{1,C_6H_5O^-}[C_6H_5O^-]}{k_{1,C_6H_5OH}[C_6H_5OH]} = 0.01$

For half life estimation purpose it is safe to assume

$$k_{1,phenol_T}[phenol_T] \approx k_{1,C_6H_5OH}[C_6H_5OH]$$

and
 $[phenol_T] \approx [C_6H_5OH]$

Thus,

$$\begin{aligned} k_{1,phenol_T} &\approx k_{1,C_6H_5OH} = k_{2,C_6H_5OH} \begin{bmatrix} {}^1O_2 \end{bmatrix}_{ss} \\ &= 10^7 \ M^{-1}s^{-1} \cdot 10^{-13} \ M = 10^{-6} \ s^{-1} \end{aligned}$$

$$t_{1/2,phenol_T} = \frac{ln2}{10^{-6} \, s^{-1}} \cdot \frac{1}{86400 \, s/d} = \mathbf{8.0} \, \mathbf{d}$$

Photochemical reactions II: Direct photolysis - kinetics

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

 $W_0(\lambda) \otimes W(\lambda)$ = 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

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



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

 $\alpha_{\rm D}(\lambda)$ = 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

And *l* is a function of λ



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*, $I_a(\lambda)$:

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

 $= k_{a}(\lambda) \cdot C_{i}$ $I_{a}(\lambda) \text{ in einstein/L-s}$ $W_{0}(\lambda) \text{ in <u>millieinstein/cm^{2}-s}$ $\epsilon_{i}(\lambda) = \text{molar absorption coeff. for compound i (L/mole-cm)}$ $C_{i} = \text{concentration of compound i (mole/L)}$ $k_{a}(\lambda) = \underline{\text{specific light absorption rate (einsten/mole-s)}}$ </u>

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 $\alpha_D(\lambda) z_{mix} \leq 0.02$

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

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

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

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

$$\left[\begin{array}{c}\text{Define}\\Z(\lambda) = \frac{W_{0}(\lambda) \cdot \alpha_{D}^{0}(\lambda)}{\alpha(\lambda)} = W_{0}(\lambda) \cdot D^{0}(\lambda)\\(Z(\lambda) \text{ has a unit of millieinstein/cm^{2}/s)}\right]$$

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

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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 constant (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

Calculate k_a^{0} of para-nitro-acetophenone (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)	λ 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 Irradiance		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	
				$k_a^0 = \sum k_a^0(\lambda) = 14.5 \cdot 10^{-3}$ einstein (mol·PNAP) ⁻¹ s ⁻¹	

2) Nearly all light absorbed

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

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

$$1 - 10^{-\alpha_{D}(\lambda) \cdot z_{mix}} \approx 1$$
(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 constant of optically thick zone (s⁻¹)