Photochemical reactions I:
Fundamentals

Light (photon)/matter interactions

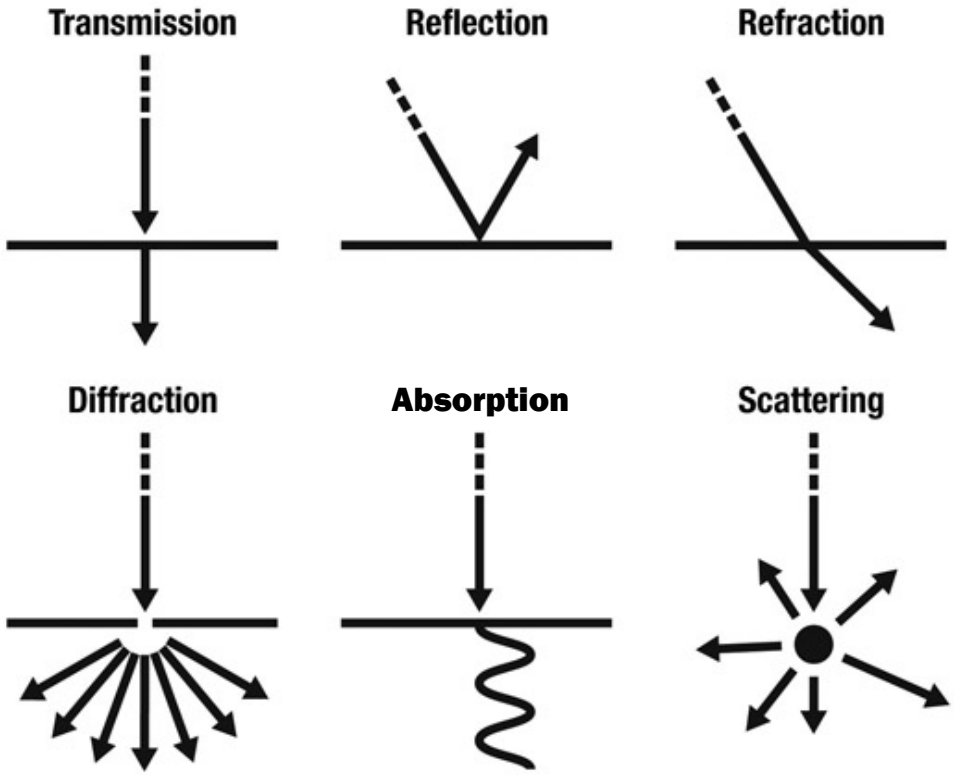
- **Photon/matter interactions play roles in**
  - Transformations in
    - the atmosphere
    - surface water
    - water & wastewater treatment (e.g., disinfection, engineered wetland)
  - Analysis
    - Light absorption $f(\lambda, C_{compound})$ – determine $C_{compound}$ by a spectrophotometer

- **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/matter interactions

- **Light interacts with matter in various ways**

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



#1

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):

  A step of a reaction of a compound occur with each photon absorbed

Photolysis – general

Molecule + photon ⟶ Molecule* ⟶ 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

Light: Source of energy

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

E = energy of a photon (J/photon)

h = 6.626 x 10^{-34} J·s, Planck constant

ν = frequency of light (s^{-1})

c = 3.0 x 10^{8} m/s, speed of light in a vacuum

λ = wavelength of light (m)

On a molar basis,

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

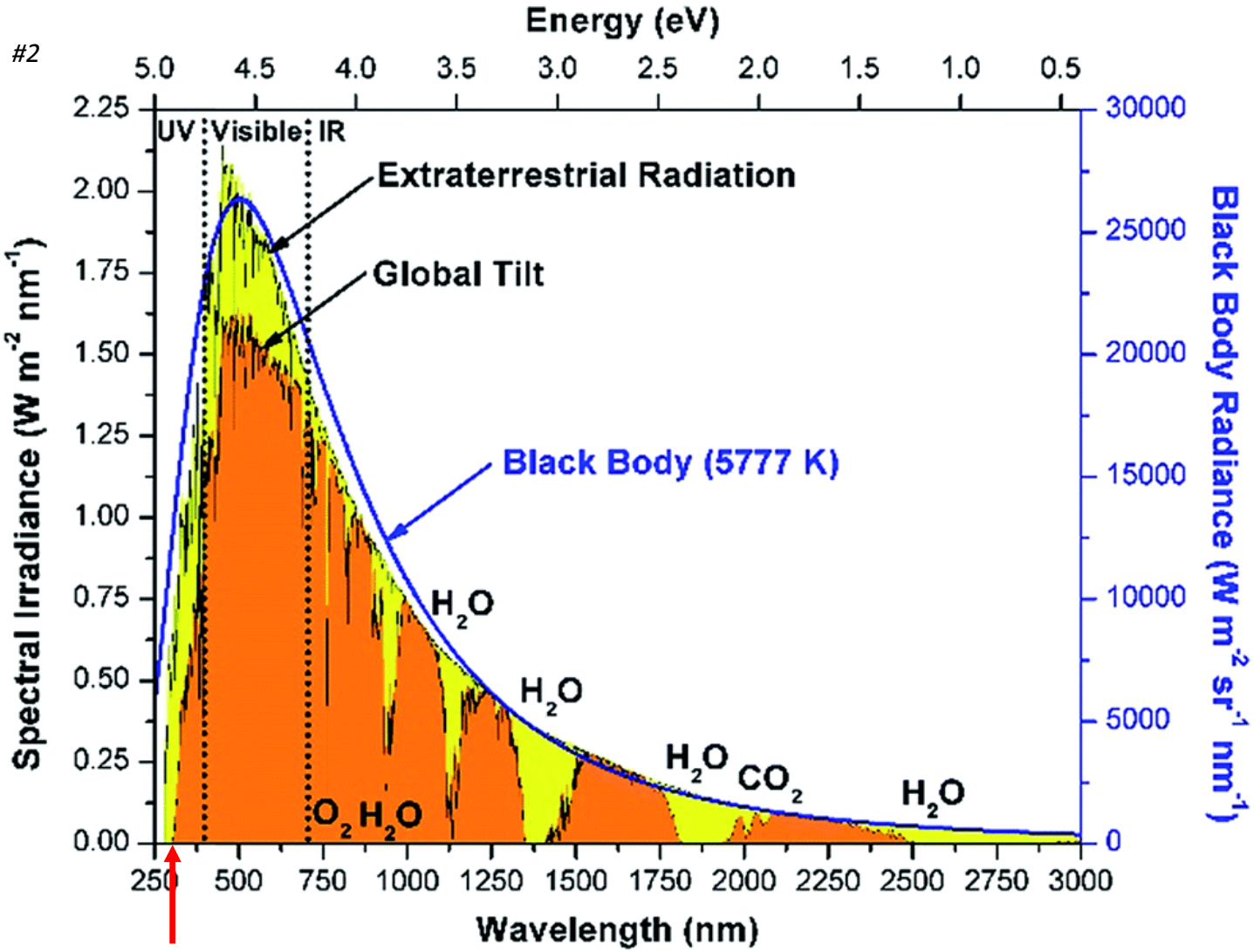
E *= energy of light on a molar basis (kJ/einstein)*

einstein: 1 mole of photons

λ = wavelength of light in nm

Solar flux & absorption

#2



Drop off of intensity below 290 nm

Bond energies & light absorption

Table 15.1 Typical Energies for Some Single Bonds and the Approximate Wavelengths of Light Corresponding to This Energy [a]

Bond	Bond Energy E [b] (kJ·mol^{-1})	Wavelength λ (nm)
O–H	465	257
H–H	436	274
C–H	415	288
N–H	390	307
C–O	360	332
C–C	348	344
C–Cl	339	353
Cl–Cl	243	492
Br–Br	193	620
O–O	146	820

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

- Compare to:

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

- Energy of UV/visible light ~ covalent bonds

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

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***

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

A = absorbance

I_0 & I = light intensity at x=0 & l, respectively (e.g., in einstein/cm^2-s)

α = absorption coefficient of the solvent (cm^{-1})

ε_i = molar absorption coefficient for solute i (M^{-1}·cm^{-1})

C_i = concentration of solute i (M)

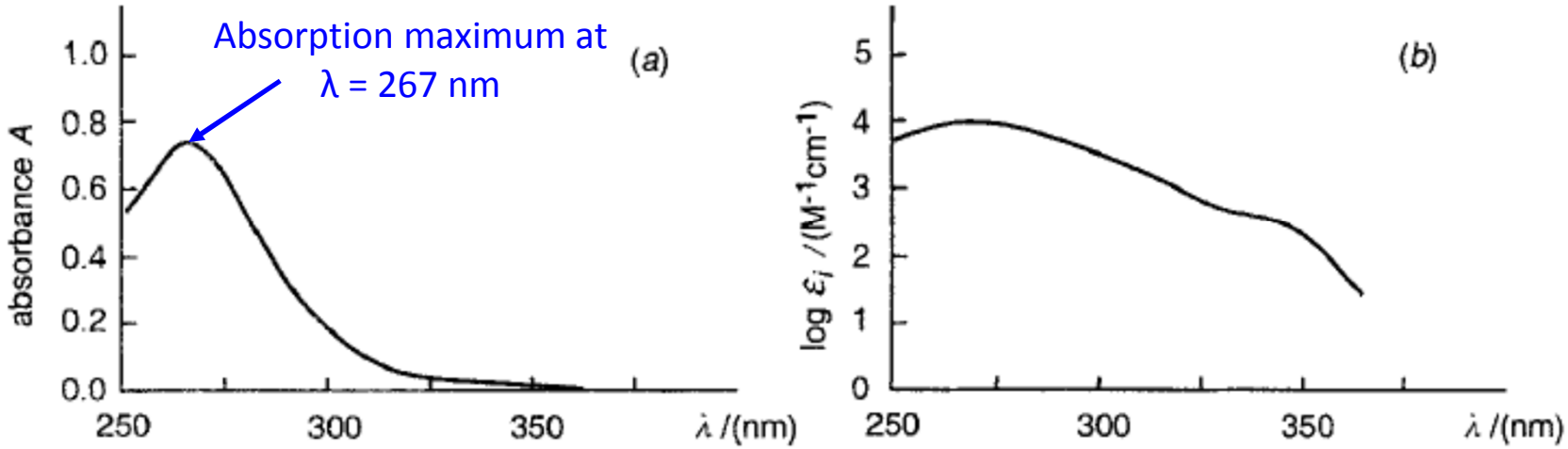
l = path length of light (cm)

Absorption spectrum

- Absorption spectrum easily measurable by UV-Vis spectrophotometer

0.1 mM nitrobenzene in aqueous solution

#4



Measure absorbance at each λ

Calculate molar extinction coefficient at each λ

Chromophores & light absorption

Chromophore	λ_{max}, nm	ε @ λ_{max}	Transition
C–C	<180	1,000	σ → σ*
C–H	<180	1,000	σ → σ*
C=C	180	10,000	π → π*
C=C–C=C	220	20,000	π → π*
C=C–C=O	220	20,000	π → π*
Benzene	260	200	π → π*
Phenol	275	1,500	π → π*
Aniline	380	10,000	π → π*
Ar-NO_2	280	7,000	π → π*
Naphthalene	310	200	π → π*
Anthracene	380	10,000	π → π*
Indole	290	5,000	π → π*
RS-SR	300	300	n → σ*
C=N	<220	20	n → π*
C=O	280	20	n → π*
N=O	300	100	n → π*
N=N	350	100	n → π*
C=C–C=O	350	30	n → π*
Benzoquinone	370	500	n → π*
N=O	660	200	n → π*

- **Chromophore**

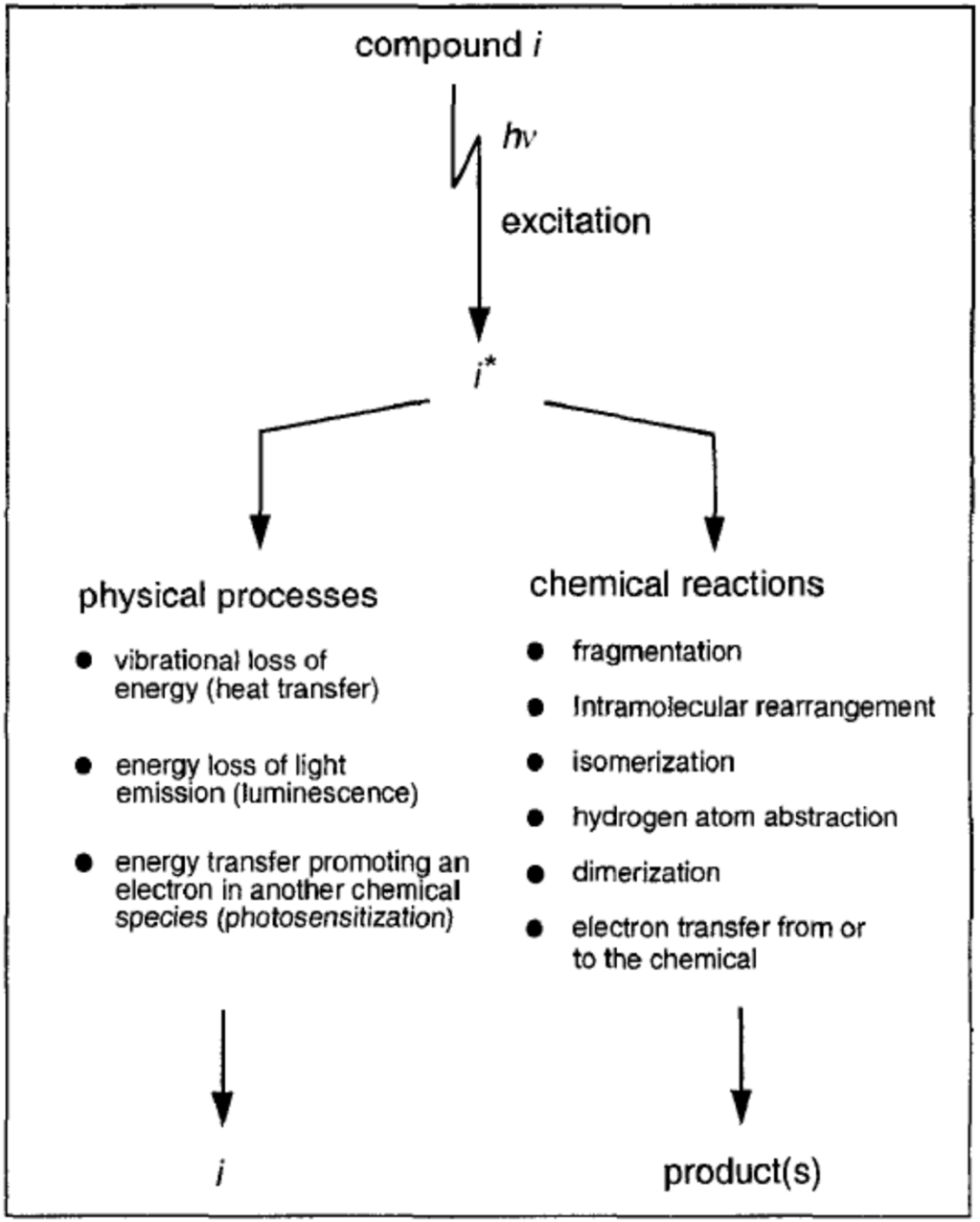
  A structural moiety that exhibits a characteristic UV/Vis absorption spectrum

- 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?



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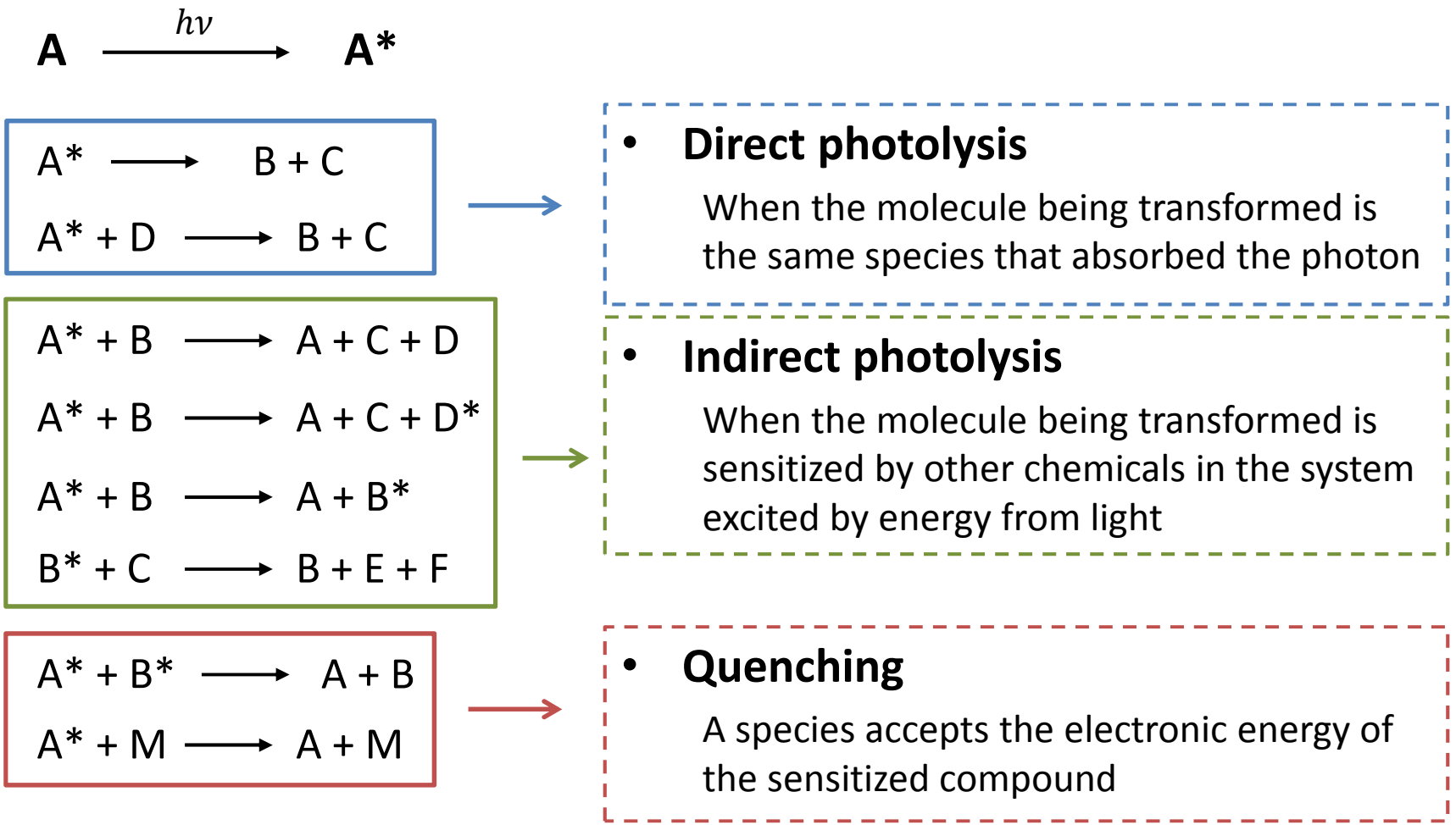
When molecule A absorbs a photon



Direct photolysis

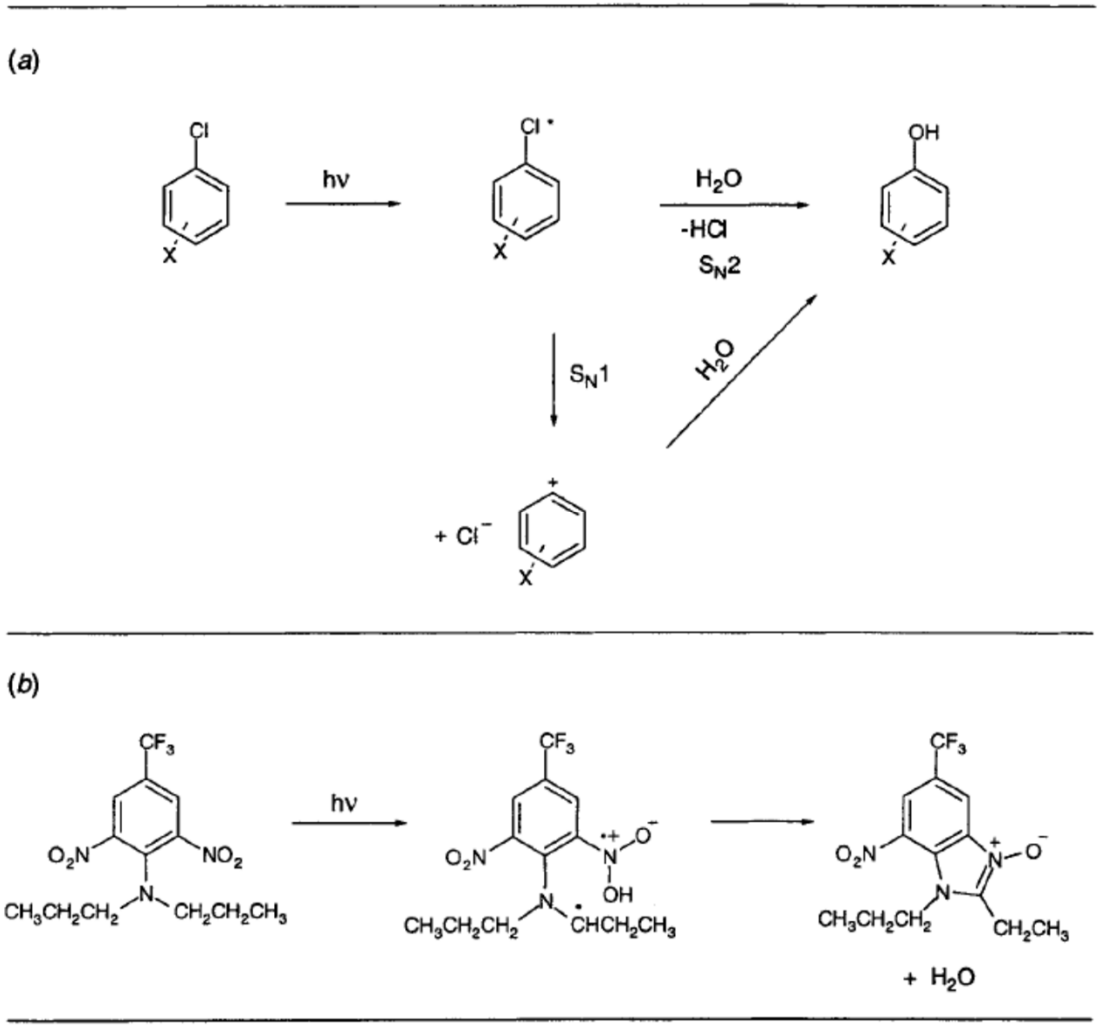


Figure 15.7 Examples of direct photochemical reaction pathways: (*a*) substituted chlorobenzenes, (*b*) trifluralin, and (*c*) a ketone (from Mill and Mabey, 1985).

Direct photolysis

(*c*)

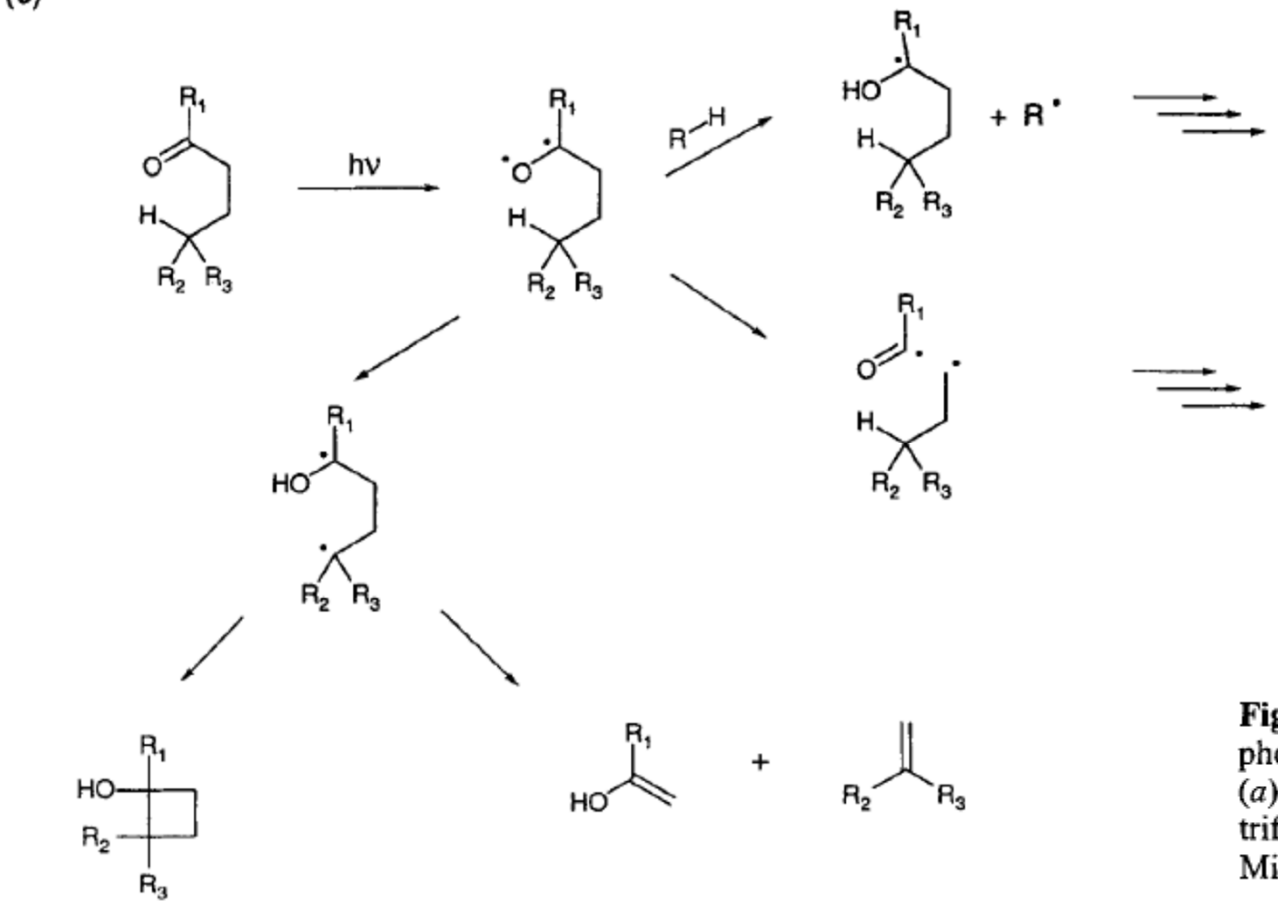


Figure 15.7 Examples of direct photochemical reaction pathways: (*a*) substituted chlorobenzenes, (*b*) trifluralin, and (*c*) a ketone (from Mill and Mabey, 1985).

#6

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, $\boldsymbol{\Phi(\lambda)}$**
  - Moles of compound transformed per moles of photons absorbed by the compound
    - Pathway specific or overall yields
      - Φs are often <<1; 10^{-2} – 10^{-6}

Quantum yield, $\Phi(\lambda)$

- **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)**

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

- **Quantum yields have to determined by experiments**

References

#1) http://weeklysciencequiz.blogspot.com/2011/09/when-light-meets-matter.html

#2) Herron, J. A., Kim, J., Upadhye, A. A., Huber, G. W., Maravelias, C. T. (2015) A general framework for the assessment of solar fuel technologies. Energy & Environmental Science 8:126-157.

#3-#6) Schwarzenbach, R., Gschwend, P. M., Imboden, D. M. (2003) Environmental Organic Chemistry, 2nd ed., John Wiley & Sons, p. 615; p. 616; p. 624; p. 625.

Photochemical reactions II:

Direct photolysis - kinetics

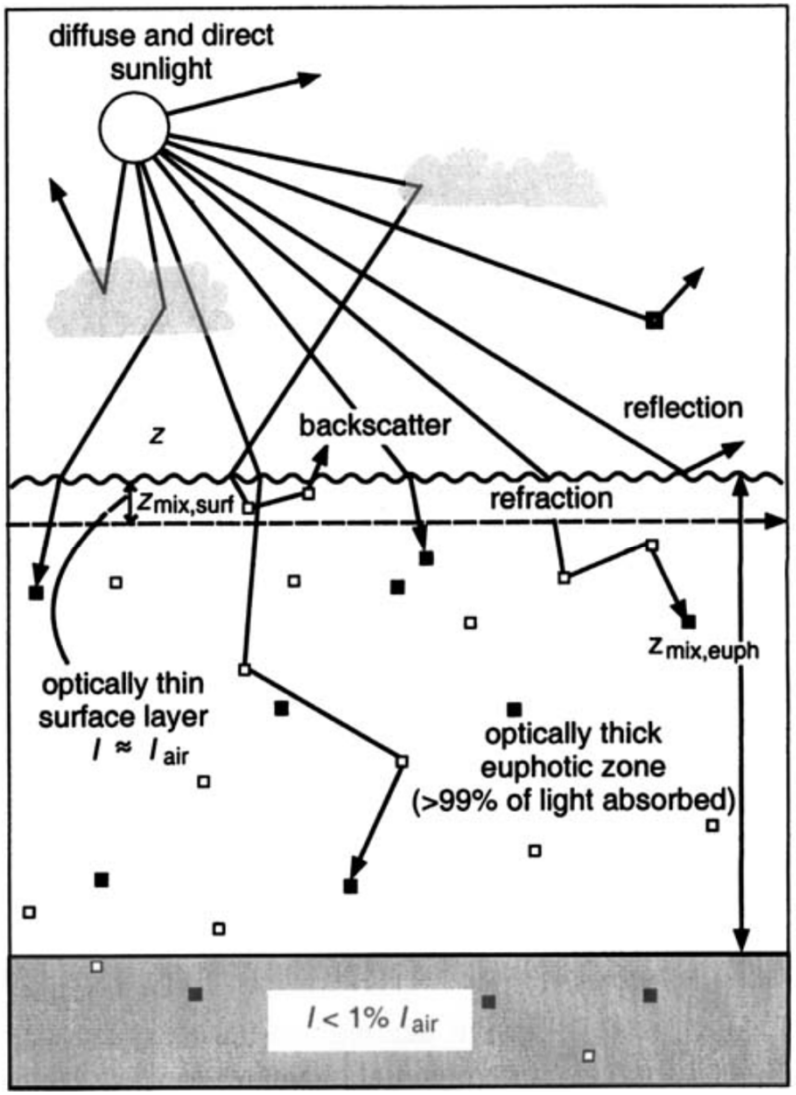
Direct photolysis – light absorption

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

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

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



Direct photolysis – light absorption

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

$\alpha_D(\lambda)$ = diffuse attenuation coefficient (cm^{-1})

$z_{mix} = V/A$ = depth of mixed water body (cm)

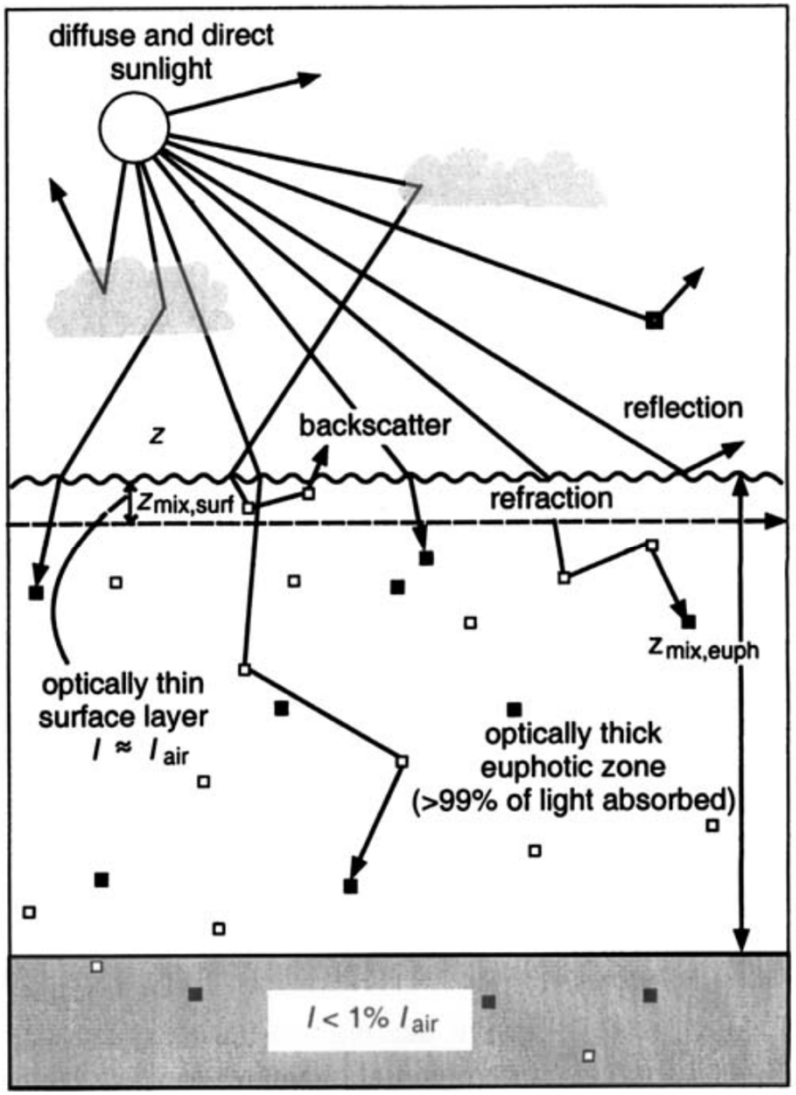
V = volume of the water body (cm^3)

A = surface area of the water body (cm^2)

$l \neq z_{mix}$ 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



Direct photolysis – light absorption

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

Define $D(\lambda)$ as: $D(\lambda) = \dfrac{l(\lambda)}{z_{mix}}$

$\alpha_D(\lambda) = D(\lambda)\alpha(\lambda)$

$D(\lambda)$ = 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

Direct photolysis – light absorption

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/cm^2-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/cm^3-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*:

$$F_i =$$

Direct photolysis – light absorption

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*, $I_a(\lambda)$:

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

$$= k_a(\lambda)\cdot C_i$$

$I_a(\lambda)$ in einstein/L-s
$W_0(\lambda)$ in millieinstein/cm²-s
$\epsilon_i(\lambda)$ = molar absorption coeff. for compound i (L/mole-cm)
C_i = concentration of compound i (mole/L)
*$k_a(\lambda)$ = **specific light absorption rate** (einsten/mole-s)*

Direct photolysis rate at specific λ

(Photolysis rate) = (Light absorption rate) x (Transformation rate when light is absorbed)

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

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

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

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

$k_p(\lambda)$ = ***the direct photolysis 1st-order rate constant at 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 = ***the overall direct photolysis 1st-order rate constant*** *(s^{-1})*

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

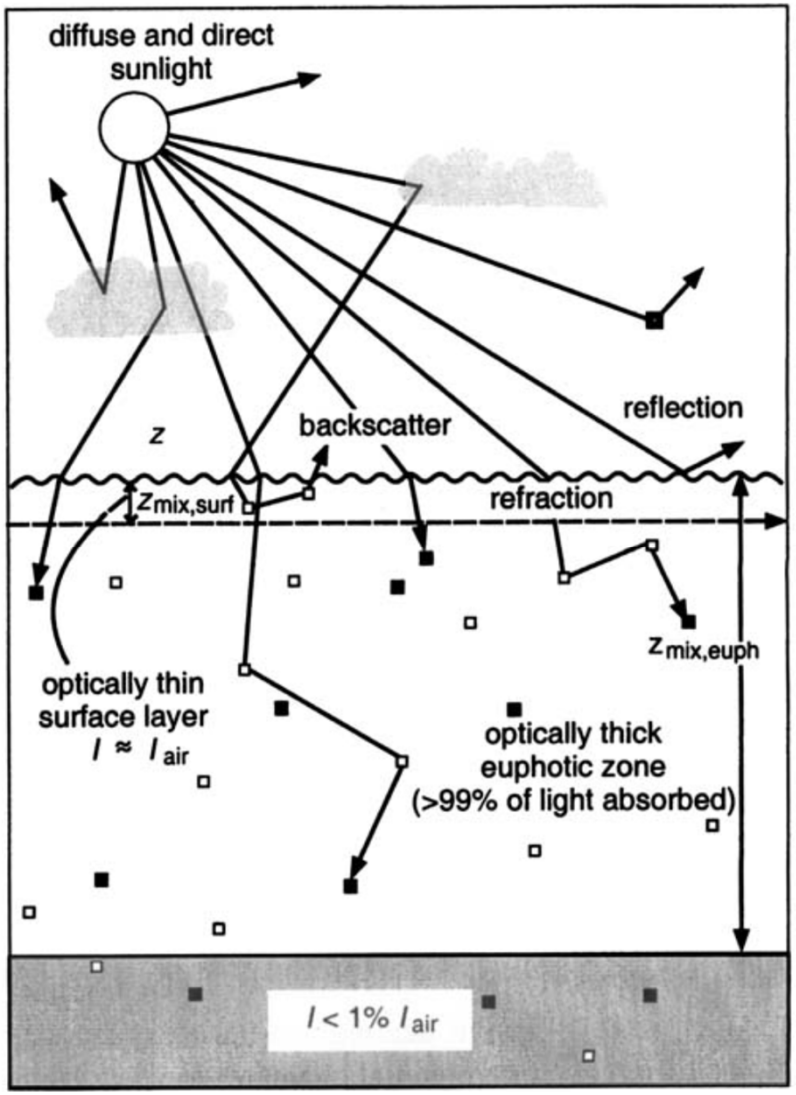
$$-\frac{dC_i}{dt} = \Phi_{ir}\left[\sum_{\lambda} k_a(\lambda)\right] C_i = \Phi_{ir} k_a C_i$$

k_a = ***the overall specific light absorption rate*** *(einsten/mole-s)*

Direct photolysis – natural water

- Two limiting cases:
  1) **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 $\boldsymbol{\alpha_D(\lambda) z_{mix} \leq 0.02}$

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

$$= \left[\sum_{\lambda} \frac{\Phi_{ir}(\lambda) \cdot W_0(\lambda) \cdot \epsilon_i(\lambda) \cdot \left[1 - 10^{-\alpha_D(\lambda) \cdot z_{mix}}\right]}{z_{mix} \cdot \alpha(\lambda)}\right] C_i$$

$$1 - 10^{-\alpha_D(\lambda) \cdot z_{mix}} \approx 2.303 \alpha_D(\lambda) \cdot z_{mix}$$

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

$$= 2.303 \left[\sum_{\lambda} \frac{\Phi_{ir}(\lambda) \cdot W_0(\lambda) \cdot \epsilon_i(\lambda) \cdot {\alpha_D}^0(\lambda)}{\alpha(\lambda)}\right] C_i$$

$$= 2.303 \left[\sum_{\lambda} Z(\lambda) \cdot \epsilon_i(\lambda) \cdot \Phi_{ir}(\lambda)\right] C_i$$

Define

$$Z(\lambda) = \frac{W_0(\lambda) \cdot {\alpha_D}^0(\lambda)}{\alpha(\lambda)} = W_0(\lambda) \cdot D^0(\lambda)$$

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

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})

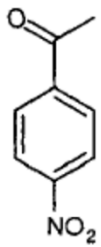
If Φ_{ir} is not a function of λ, then:

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

${k_a}^0$= 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.



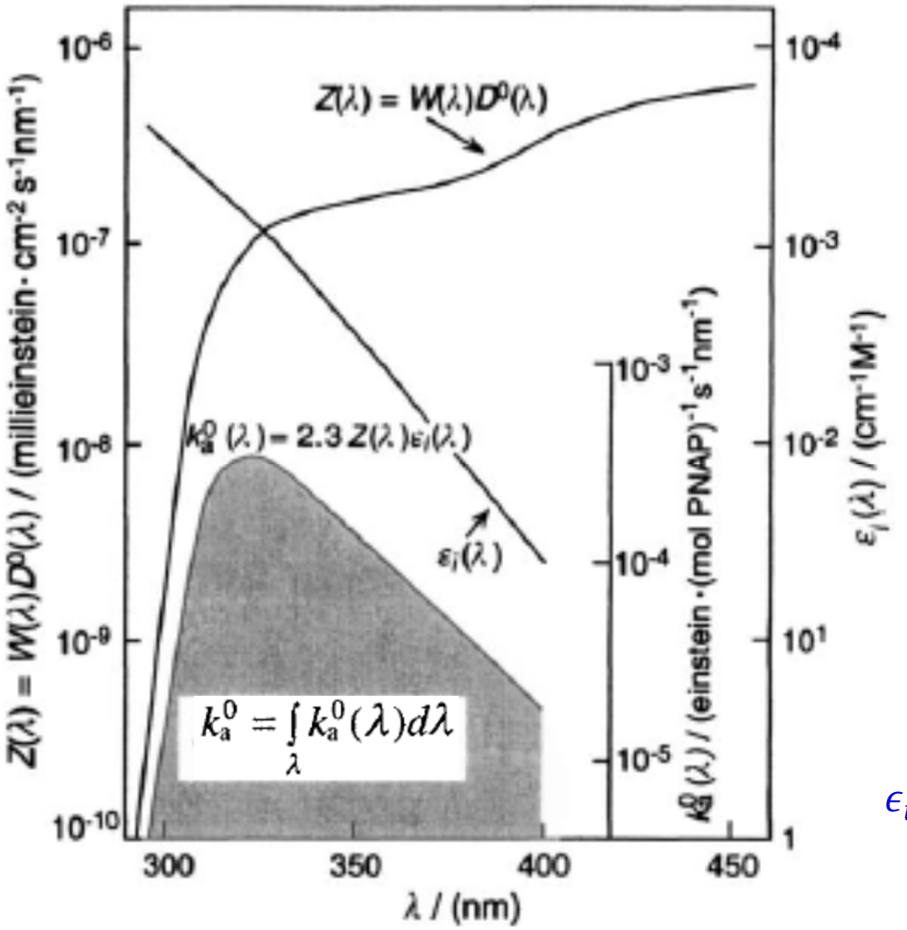
para-nitro-acetophenone (PNAP)

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

$Z(noon, \lambda) = W(noon, \lambda) \cdot D^0(\lambda)$, $D^0(\lambda)$ 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)	(millieinstein·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 – $k_a{}^0$



Obtain $k_a{}^0$ by

$$k_a{}^0 = \int k_a{}^0 d\lambda = 2.3 \int Z(\lambda)\epsilon_i(\lambda)\, d\lambda$$

$$\approx 2.3 \sum Z(\lambda)\epsilon_i(\lambda)$$

$\epsilon_i(\lambda)$ is obtained from experiments

#3

Realistic example – $k_a{}^0$

	Solar Irradiance		PNAP	
λ (Center) (nm)	λRange ($\Delta\lambda$) (nm)	$Z(\text{noon},\lambda)$ [a] (millieinstein · 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}

#4

2) Nearly all light absorbed

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

$$-\frac{dC_i}{dt} = \left[\sum_{\lambda} \frac{\Phi_{ir}(\lambda) W_0(\lambda) \cdot \epsilon_i(\lambda) \cdot \left[1 - 10^{-\alpha_D(\lambda) \cdot z_{mix}}\right]}{z_{mix} \cdot \alpha(\lambda)}\right] C_i$$

$$1 - 10^{-\alpha_D(\lambda) \cdot z_{mix}} \approx 1$$

(when $\alpha_D(\lambda) z_{mix} \geq 2$)

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

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

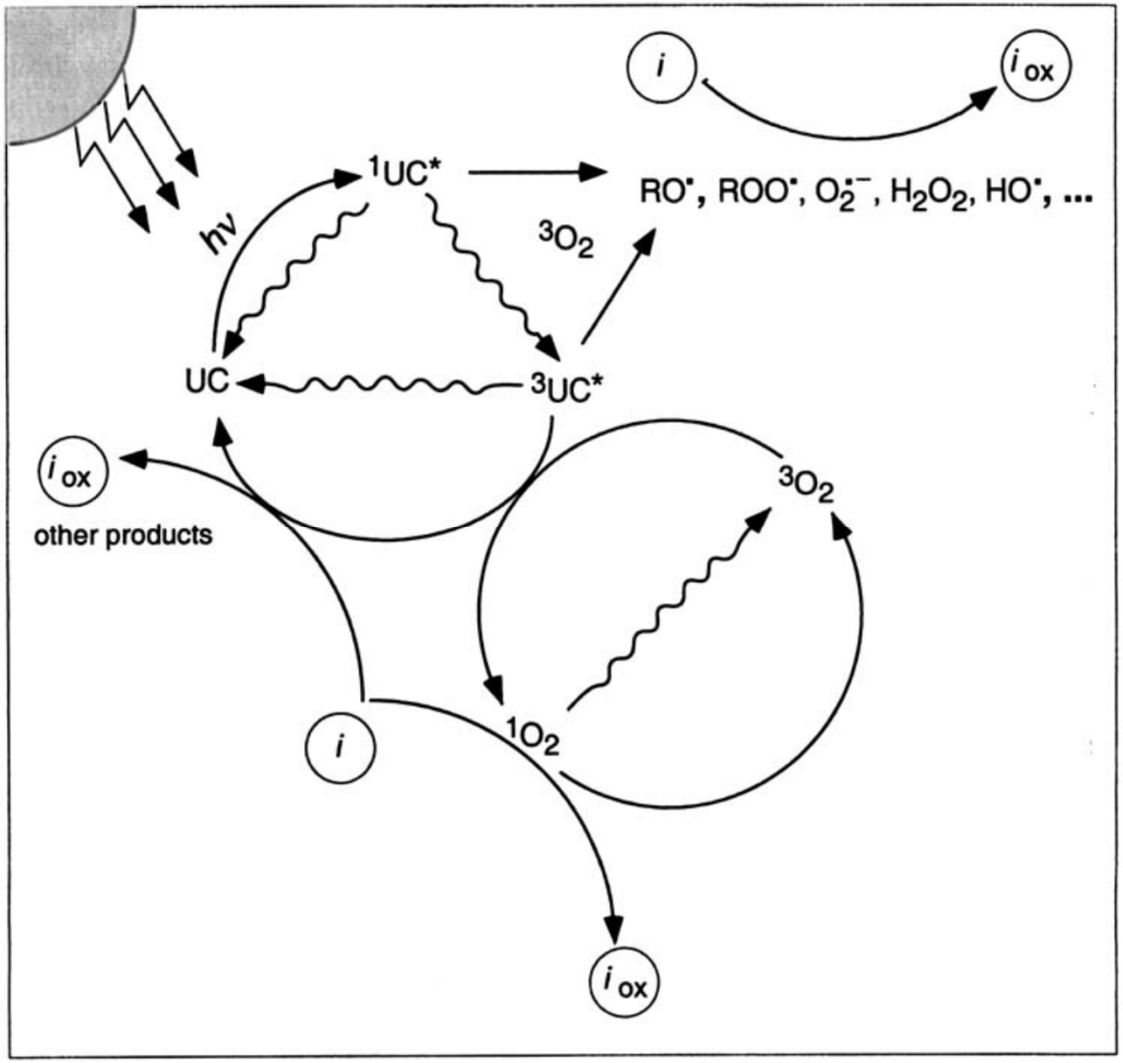
References

#1-#4) Schwarzenbach, R., Gschwend, P. M., Imboden, D. M. (2003) Environmental Organic Chemistry, 2nd ed., John Wiley & Sons, p. 628; p. 632; p. 634; p. 635.

Photochemical reactions III:

Indirect photolyis

Indirect (sensitized) photolysis



- UC: Unknown chromophore

  ex) colored DOM (CDOM)
- Singlet oxygen ($^1O_2$): excited state
- Triplet oxygen ($^3O_2$): 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	$^1O_2$	Sensitized by excited DOM
Superoxide anion	$O_2^{-\bullet}$	Photolysis of Fe(III) complexes; deprotonation of $HO_2^\bullet$
Hydroperoxyl radical	$HO_2^\bullet$	Uptake from atmosphere, protonation of $O_2^{-\bullet}$
Hydrogen peroxide	H_2O_2	Photolysis of Fe(III) complexes; disproportionation of superoxide anion
Ozone	O_3	Uptake from atmosphere
Hydroxyl radical	$^\bullet OH$	Photolysis of Fe(III) complexes;, H_2O_2, NO_3^-, NO_2^-; decomposition of O_3
Organic peroxy radicals	$ROO^\bullet$	Photolysis of DOM
Aquated electron	e^-_{eq}	Photolysis of DOM

Steady-state concentrations of PPRIs

#2

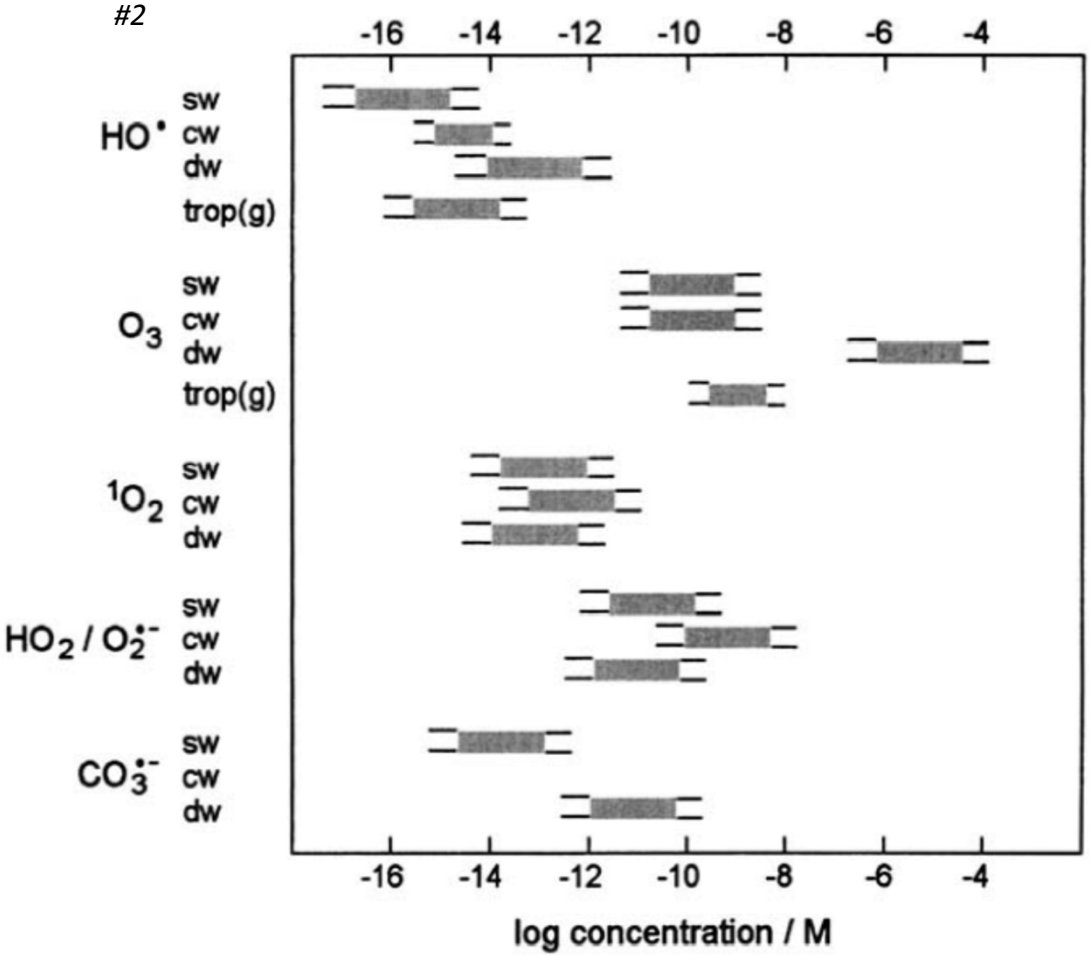
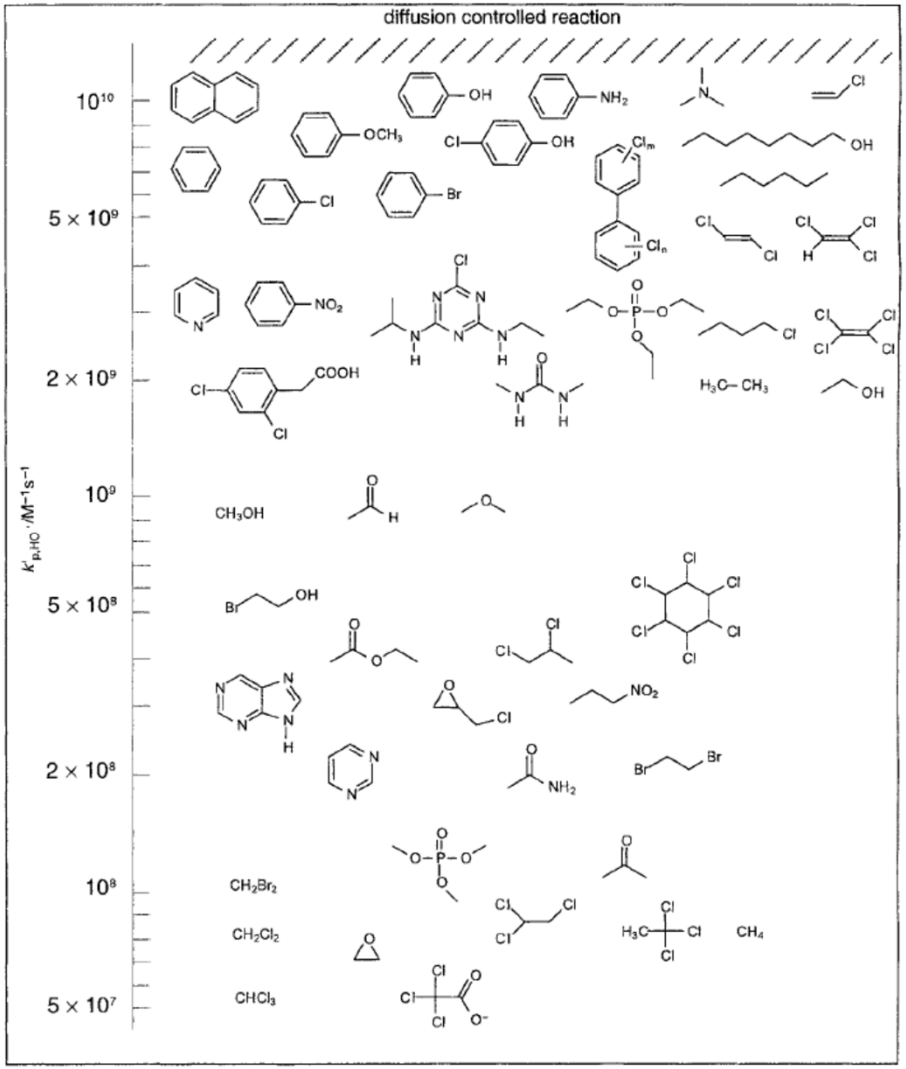


Figure 16.1 Ranges of steady-state concentrations of reactive oxygen species in sunlit surface waters (sw), sunlit cloud waters (cw), drinking-water treatment (dw), and the troposphere (trop(g)). Data from Sulzberger et al. (1997) and Atkinson et al. (1999).

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

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

References

#1-#3) Schwarzenbach, R., Gschwend, P. M., Imboden, D. M. (2003) Environmental Organic Chemistry, 2nd ed., John Wiley & Sons, p. 659; p. 657; p. 664.

Photochemical reactions IV:

Exercise

Direct photolysis: For cmpd w/ speciation

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):

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

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

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

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

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

Direct photolysis: For cmpd w/ speciation

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^-]:

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

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

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

Then:

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

From (1)-(3):

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

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

Now, recall from acid-base equilibrium:

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

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}:

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

$$= 0.289 \times 0.495\ d^{-1} + (1 - 0.289) \times 0.259\ d^{-1} = 0.327\ d^{-1}$$

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

$$t_{1/2} = \frac{ln2}{k} = \frac{ln2}{0.327\ d^{-1}} = \mathbf{2.1\ days}$$

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, λ) (millieinstein/cm^2-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

Direct photolysis: For multiple wavelengths

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. ($\varepsilon_i(\lambda)$; $M^{-1}cm^{-1}$)***	***Z(24 h, λ) × $\varepsilon_i(\lambda)$***
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 × 10^3 cm³/L
= einstein/mol-d

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

$$= 2.303 \times (30.31\ einstein/mol - d) \times (2.9 \times 10^{-3}\ \ mol/einstein)$$

$$= 0.202\ d^{-1}$$

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