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



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 \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

Light: Source of energy

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

E = energy of a photon (J/photon) $h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s}, Planck \text{ constant}$ $v = frequency of light (s^{-1})$ $c = 3.0 \times 10^8 \text{ m/s}, \text{ speed of light in a vacuum}$ $\lambda = wavelength of light (m)$

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 <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

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

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

Absorption spectrum

• Absorption spectrum easily measurable by UV-Vis spectrophotometer



0.1 mM nitrobenzene in aqueous solution

Chromophores & light absorption

Chromophore	λ_{max} , nm	ε@λ _{max}	Transition
C–C	<180	1,000	$\sigma \rightarrow \sigma^*$
С–Н	<180	1,000	$\sigma \rightarrow \sigma^*$
C=C	180	10,000	$\pi \rightarrow \pi^*$
C=C-C=C	220	20,000	$\pi \rightarrow \pi^*$
C=C-C=O	220	20,000	$\pi \rightarrow \pi^*$
Benzene	Benzene 260		$\pi \rightarrow \pi^*$
Phenol	275	1,500	$\pi \rightarrow \pi^*$
Aniline	380	10,000	$\pi \rightarrow \pi^*$
Ar-NO ₂	280	7,000	$\pi \rightarrow \pi^*$
Naphthalene	310	200	$\pi \rightarrow \pi^*$
Anthracene	380	10,000	$\pi \rightarrow \pi^*$
Indole	290	5,000	$\pi \rightarrow \pi^*$
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

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

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

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

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

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

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

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

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

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

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

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

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; $10^{-2} 10^{-6}$

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

Nucleophilic reactions III: Hydrolysis of esters, etc.

Hydrolysis of carboxylic & carbonic acid derivatives

- Carboxylic acid derivatives
- Carbonic acid derivatives



- Unsaturated, electron-deficient C
- Reacts predominantly with H₂O & OH⁻ (hydrolysis)
- General reaction mechanism

$$HO^{+} HO^{+} HC^{+} HC^{+}$$

Hydrolysis of Esters

- Three mechanisms:
 - 1) acid-catalyzed
 - 2) neutral
 - 3) base-catalyzed
- Importance of each reaction depends on the structure of the reactant



Ester hydrolysis: acid-catalyzed

- Ester carbon is protonated

 → enhanced depletion of
 electrons near the carbon
 → ester carbon gets more
 susceptible to H₂O attack
- Reaction (2) is rate limiting
- Reaction rate depends on:
 - k_A'
 - K_a of the protonated ester
 - [H⁺]



Ester hydrolysis: base-catalyzed

• (1) only or both (1) & (2) can be rate-limiting

- Rate depends on [OH⁻] and in addition:
 - If only (1) is rate-limiting: — Depends on the formation of $R_1 - c_{-} - R_2$

If both (1) & (2) are rate-limiting: – Depends on the formation of $R_1 - c - 0 - R_2$ & the property of the leaving group

 $R_1 - C = \begin{pmatrix} 0 \\ -R_2 \end{pmatrix} + HO^2 = \begin{pmatrix} k_{B1} \text{ (slow)} \\ k_{B2} \text{ (fast)} \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \\ R_1 - C - O - R_2 \end{pmatrix}$

 $R_{1} - C - O - R_{2} \qquad \frac{k_{B3} (fast...slow)}{k_{B4} (slow)} \qquad R_{1} - C O + O - R_{2} \qquad (2)$ $R_{1} - C O + O - R_{2} \qquad \frac{(fast)}{(fast)} \qquad R_{1} - C O + HO - R_{2} \qquad (3)$

(1)

Ester hydrolysis: neutral



- Similar to base-catalyzed
- The property of the leaving group is more important for H₂O (weaker nucleophile) than OH⁻

Ester hydrolysis kinetics

• k_h : pseudo-first-order hydrolysis rate constant (s⁻¹), f(pH)

$$k_{h} = k_{A}[H^{+}] + k_{H_{2}O}[H_{2}O] + k_{B}[OH^{-}]$$
$$= k_{A}[H^{+}] + k_{N} + k_{B}[OH^{-}]$$

• Hydrolysis half-life (at certain pH)

$$t_{1/2 \ (hydroysis)} = \frac{\ln 2}{k_h}$$

Ester hydrolysis: / values



I_{IJ} = the pH value at which the rates for I and J reactions are the same I, J: A (acid-catalyzed); N (neutral); B (base-catalyzed)

F	Compound O II $B_1 - C - O - B_2$							
\mathbf{R}_1	R ₂	$k_{\rm A}$ (M ⁻¹ s ⁻¹)	k_{N} (s ⁻¹)	$k_{\rm B} \over ({ m M}^{-1} { m s}^{-1})$	<i>t</i> _{1/2} (pH 7)	I _{AN} b,c.e	I _{AB} ^{c,e}	I _{NB} ^{d,e}
CH ₃ CH ₃	- CH ₂ CH ₃ - C(CH ₃) ₃	1.1×10^{-4} 1.3×10^{-4}	1.5×10^{-10}	1.1×10^{-1} 1.5×10^{-3}	2 yr 140 yr	(5.9)	5.5 6.5	(5.1)
H	-C(CH ₃) ₃	2.7×10^{-3}	$1.0 imes 10^{-6}$	1.7×10^{0}	7 d	2.6	5.6	7.8
CH ₃ –	$-CH = CH_2$	1.4×10^{-4}	1.1×10^{-7}	1.0×10^1	7 d	3.1	(4.6)	6.0
CH3 -	\neg	$7.8 imes 10^{-5}$	$6.6 imes 10^{-8}$	1.4×10^{0}	38 d	3.1	(4.8)	6.7
CH ₃ –			1.1×10^{-5}	9.4×10^{1}	10 h			7.1
CH_2Cl-	– CH ₃	$8.5 imes 10^{-5}$	$2.1 imes 10^{-7}$	1.4×10^2	14 h	2.6	(3.9)	5.2
CHCl ₂ -	$-CH_3$	$2.3 imes 10^{-4}$	$1.5 imes 10^{-5}$	$2.8 imes 10^3$	40 min	1.2	(3.5)	5.7
CHCl ₂ –	$-\langle \rangle$		$1.8 imes 10^{-3}$	$1.3 imes 10^4$	4 min			7.1

Table 13.8 Rate Constants k_A , k_N , and k_B , Half-Lives at pH 7, and I Values for Hydrolysis of Some Carboxylic Acid Esters at 25°C^{*a*}

^{*a*} Data from Mabey and Mill (1978) except for *tert*-butyl formate ($R_1 = H, R_2 = C(CH_3)_3$; Church et al., 1999). ^{*b*} $I_{AN} = \log (k_A/k_N)$. ^{*c*} $I_{AB} = 1/2 \log (k_A/k_BK_w)$. ^{*d*} $I_{NB} = \log (k_N/k_BK_w)$. ^{*e*} Parentheses indicate that one or both of the processes is too slow to contribute significantly to the overall rate.

Nucleophilic reactions: Exercise

S_N2: Relative nucleophilicity

Q: Estimate the half-life (in days) of CH_3Br present at low concentration (i.e., < 0.01mM) in a homogeneous aqueous solution (pH=7.0, T=25°C) containing 100 mM Cl⁻, 2 mM NO₃⁻, 1 mM HCO₃⁻, and 0.1 mM CN⁻. In pure water at pH 7.0 and 25°C, the half-life of CH_3Br is about 20 days.

Solution)

Nucleophile concentrations are all in excess compared to CH₃Br concentration



For a nucleophile with a concentration much lower than [Nu]_{50%}, we can neglect its contribution (it should contribute much less than H_2O)

$$[CI^{-}] = 0.1; [NO_{3}^{-}] = 2 \times 10^{-3}; [HCO_{3}^{-}] = 10^{-3};$$

$$[CN^{-}] = 10^{-4}; [OH^{-}] = 10^{-7} (units in M)$$

$$NO_{3}^{-} \& OH^{-} can be neglected.$$

$$log\left(\frac{k_{Nu}}{k_{H_2O}}\right) = s \cdot n_{Nu,CH_3Br} = n_{Nu,CH_3Br}$$

s=1 for CH₃Br

$$k_{Nu} = 10^{n_{Nu,CH_3Br}} \cdot k_{H_2O}$$

Table 13.5 Calculated Concentration of Nucleophile Required to Compete with Water in an S_N2 Reaction with Alkyl Halides Assuming an s Value of 1

Nucleophile	$[Nu]_{50\%}^{a}(M)$	
NO ₃	~6	
F ⁻	$\sim 6 \times 10^{-1}$	
SO4 ²⁻	$\sim 2 \times 10^{-1}$	
CI-	$\sim 6 \times 10^{-2}$	
HCO ₃	$\sim 9 \times 10^{-3}$	
HPO ₄	$\sim 9 \times 10^{-3}$	
Br ⁻	$\sim 7 \times 10^{-3}$	
OH-	$\sim 4 \times 10^{-3}$	
I_	$\sim 6 \times 10^{-4}$	
HS ⁻	$\sim 4 \times 10^{-4}$	
CN ⁻	$\sim 4 \times 10^{-4}$	
$S_2O_3^{2-}$	$\sim 4 \times 10^{-5}$	
S42-	$\sim 4 \times 10^{-6}$	

^{*a*} Eq. 13-5 using the $n_{\text{Nu,CH_3Br}}$ values given in Table 13.3. 13

EOC text, p. 501

$$k_{obs} = k_{H_2O} \{ [H_2O] + 10^{3.0} [Cl^-] + 10^{3.8} [HCO_3^-] + 10^{5.1} [CN^-] \}$$

= (174.2 M) \cdot k_{H_2O} Taing the second s

Half-life for a 1st order (or pseudo-1st order) reaction is given as

 $t_{1/2} = \frac{ln2}{k}$

In pure water, only hydrolysis reaction by H₂O occurs:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{k_{H_2O}[H_2O]}$$
$$k_{H_2O} = \frac{\ln 2}{t_{1/2}[H_2O]} = \frac{\ln 2}{20 \ d \cdot 55.3 \ M}$$
$$= 6.27 \times 10^{-4} \ M^{-1} d^{-1}$$

Table 13.3 Relative Nucleophilicities of Some Important Environmental Nucleophiles: n-Values Determined from the Reaction with Methyl Bromide or n-Hexyl Bromide in Water (Eq. 13-3, s = 1)

Nucleophile	$n_{\rm Nu, CH_3Br}^{a}$		
ClO ₄	<0		
H ₂ O	0		
NO ₃	1.0		
F ⁻	2.0		
SO ₄ ²⁻	2.5		
CH ₃ COO ⁻	2.7		
C1 ⁻	3.0		
HCO ₃ ,HPO ₄ ²⁻	3.8		
Br	3.9		
OH-	4.2		
I -	5.0		
CN ⁻ , HS ⁻	5.1		
$S_2O_3^{2-}$	6.1 ^b		
PhS ⁻	6.8 ^b		
S ₄ ²⁻	7.2 ^b		

^{*a*} Data from Hine (1962). ^{*b*} Data from Haag and Mill (1988a).

EOC text, p. 498

Now, we are ready to calculate the pseudo-1st order rate constant for the solution:

$$k_{obs} = (174.2 M) \cdot k_{H_2O} = 0.109 d^{-1}$$

Therefore,

$$t_{1/2} = \frac{\ln 2}{k_{obs}} = \frac{\ln 2}{0.109 \, d^{-1}} = \mathbf{6.4} \, \mathbf{d}$$

Q: Following pseudo-first order hydrolysis rate constants, k_h , were determined by a laboratory kinetic experiment for DNPA at 25°C. Determine the rate constants for the neutral (k_N) and base-catalyzed (k_B) hydrolysis of DNPA. Determine the I_{NB} .



рН	3.0	4.0	5.0	8.5
k _h (s⁻¹)	4.3 x 10 ⁻⁵	4.5 x 10 ⁻⁵	4.4 x 10 ⁻⁵	5.1 x 10 ⁻⁴

Solution)

Because k_h is almost the same at pH=3.0-5.0, acid-catalyzed hydrolysis is insignificant.

As k_h is neither a function of [H⁺] nor [OH⁻] at this range, neutral hydrolysis should be dominant at pH=5.0

 $k_h(pH = 5.0) = k_N = 4.4 \times 10^{-5} \, s^{-1}$

At pH=8.5, both neutral and base-catalyzed hydrolysis will occur:

$$k_h(pH = 8.5) = k_N + k_B[OH^-] = 5.1 \times 10^{-4} \, s^{-1}$$

$$[OH^{-}] = \frac{K_w}{[H^{+}]} = \frac{10^{-14}}{10^{-8.5}} = 10^{-5.5} M$$
 (pK_w=14 @ 25°C)

$$k_B = \frac{k_h - k_N}{[OH^-]} = \frac{(5.1 \times 10^{-4} \, s^{-1}) - (4.4 \times 10^{-5} \, s^{-1})}{10^{-5.5} \, M} = \mathbf{147} \, \mathbf{M}^{-1} \mathbf{s}^{-1}$$

At pH=I_{NB},

$$k_{N} = k_{B}[OH^{-}] = k_{B} \frac{K_{w}}{[H^{+}]}$$

$$[H^{+}] = k_{B} \frac{K_{w}}{k_{N}} = 147 \ M^{-1} s^{-1} \times \frac{10^{-14}}{4.4 \times 10^{-5} \ s^{-1}} = 3.34 \times 10^{-8} \ M^{-1}$$

$$pH = -\log[H^{+}] = 7.5$$

$$I_{NB} = 7.5$$