Transformation Reactions-2

- Redox Reactions
- Photolysis

(from Environmental Organic Chemistry by Schwarzenbach et al.)

Changha Lee

School of Chemical and Biological Engineering
Seoul National University

Chapter 14

Chemical Transformations II: Redox Reactions

14.1 Introduction, Overview

√ Definition of reduction & oxidation reactions (i.e., redox reactions)

- Oxidation: loss of e^- or H, gain of O, increase of oxidation number
- Reduction: gain of e^- or H, loss of O, decrease of oxidation number

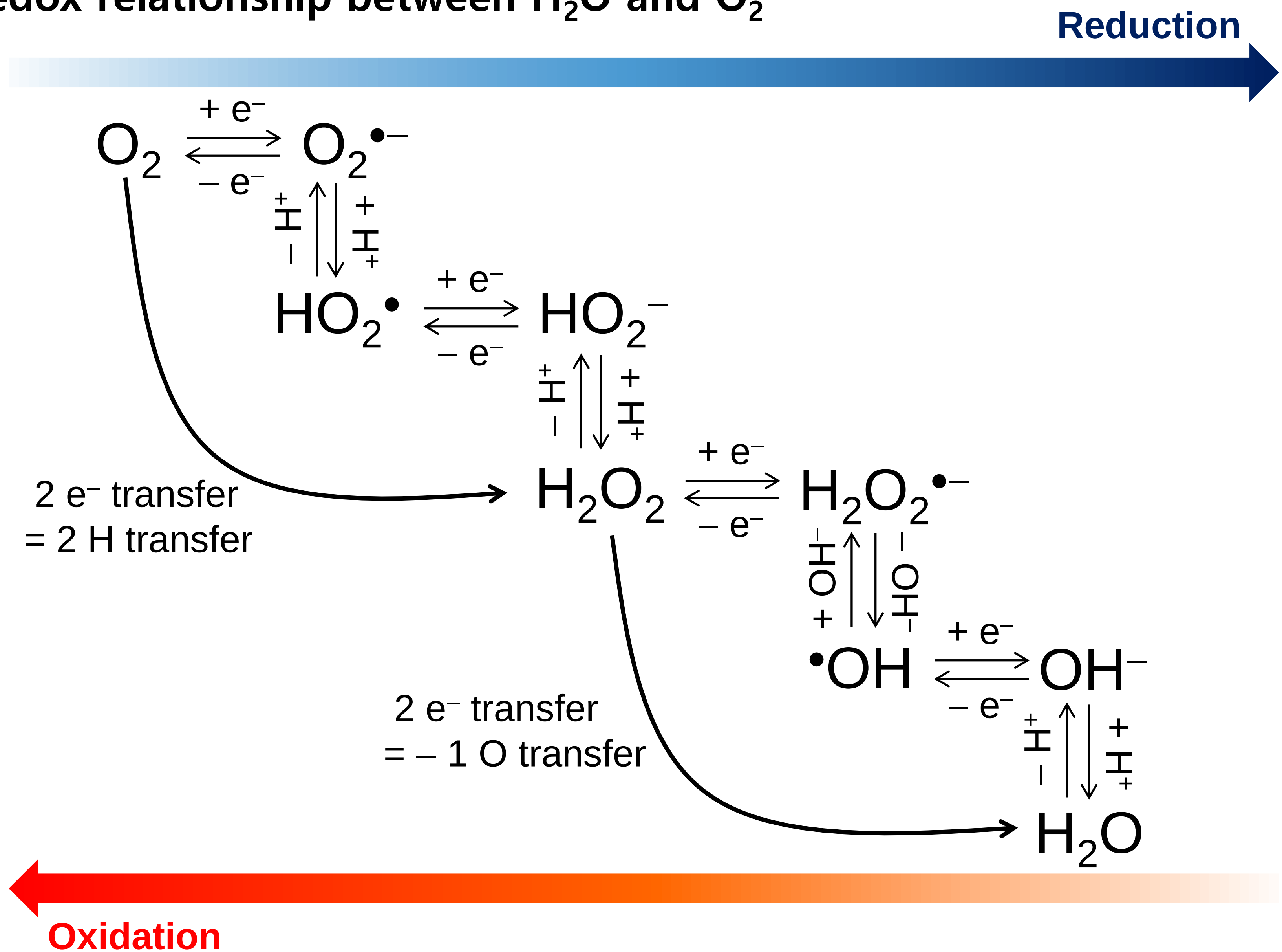
e.g., $C + H_2 \rightarrow CH_4$

$C + O_2 \rightarrow CO_2$

$Fe^0 \rightarrow Fe^{2+} + 2e^-$

DP-1

Redox relationship between H_2O and O_2



Electronegativity increases

Period																		
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.6
6	Cs 0.79	Ba 0.89	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 2.33	Bi 2.02	Po 2.0	At 2.2	Rn
7	Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo

Lanthanides	*	La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27
Actinides	**	Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.3

Table 14.1 Examples of Some Simple Redox Reactions That May Occur Chemically in the Environment [a]

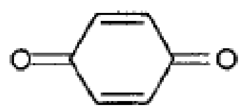
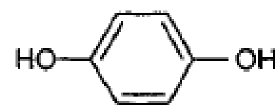
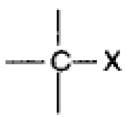
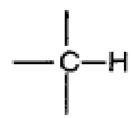
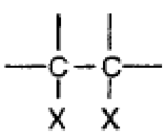
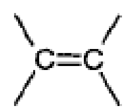
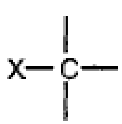
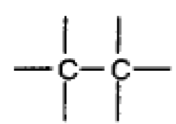
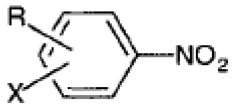
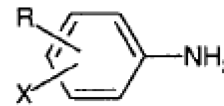
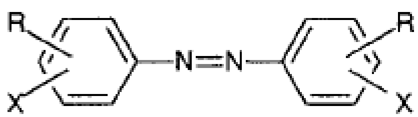
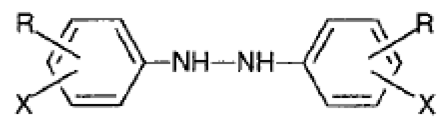
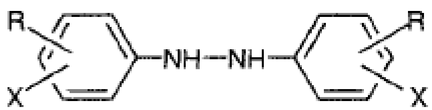
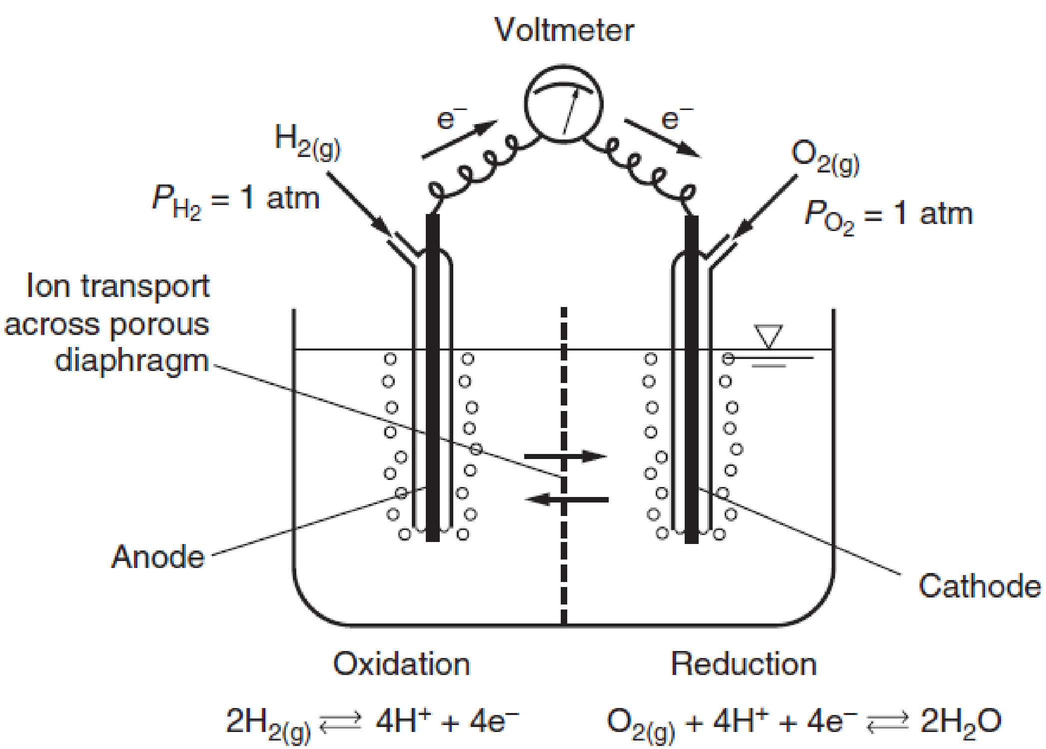
Oxidized Species	Reduction ⇌ Oxidation	Reduced Species	Equation Number
Change in Oxidation State of Carbon Atom(s)			
R—COOH + 2 H^+ + 2 e^-	←	R—CHO + H_2O	(14-4)
 + 2 H^+ + 2 e^-	⇌		(14-5)
 (X=Cl,Br,I) + H^+ + 2e^-	→	 + X^-	(14-6)
 (X=Cl,Br,I) + 2e^-	→	 + 2 X^-	(14-7)
2  (X=Cl,Br,I) + 2e^-	→	 + 2 X^-	(14-8)

Table 14.1 Examples of Some Simple Redox Reactions That May Occur Chemically in the Environment [a]

Oxidized Species	Reduction ⇌ Oxidation	Reduced Species	Equation Number
	Change in Oxidation State of Nitrogen Atom(s) [b]		
 $+ 6 H^+ + 6 e^-$	⇌	 $+ 2 H_2O$	(14-9)
 $+ 2 H^+ + 2 e^-$	⇌		(14-10)
 $+ 2 H^+ + 2 e^-$	⇌	2 	(14-11)
	Change in Oxidation State of Sulfur Atom(s) [c]		
R–S–S–R $+ 2 H^+ + 2 e^-$	⇌	2 R–SH	(14-12)
R–S(=O)–R' $+ 2 H^+ + 2 e^-$	⇌	R–S–R' $+ H_2O$	(14-13)

14.2 Thermodynamic Considerations of Redox Reactions

1. Half Reactions and (Standard) Reduction Potentials



$$O_2\,(aq) + 4H^+ + 4e^- \rightleftarrows 2H_2O \qquad \text{(reduction)} \quad E^\circ_{red} = 1.27\text{ V}$$

$$H_2 \rightleftarrows 2H^+ + 2e^- \qquad \text{(oxidation)} \quad E^\circ_{ox} = 0\text{ V}$$

√ "Reduction (redox) potential" is not for a compound, but for a reaction (or a redox couple)!

e.g.,

The reduction potential of A^{3+} is ??? V_{SHE} **X**

Because A^{3+} may go through different redox reactions with different reduction potentials.

$$A^{3+} + e^- \rightarrow A^{2+}$$
$$A^{3+} + 3e^- \rightarrow A^0$$

The reduction potential of $A^{3+} + e^- \rightarrow A^{2+}$ is ??? V_{SHE} **O**

The reduction potential of A^{3+}/A^{2+} is ??? V_{SHE} **O**

$$E^o[A^{3+}/A^{2+}] = ??? \ V_{SHE}$$ **O**

√ We can tell if a certain redox reaction is thermodynamically favored or not by reduction (redox) potentials of its half reactions!

e.g.,

$Ni^0 + Fe^{2+} \rightarrow Ni^{2+} + Fe^0$ (favored or unfavored) ?

$Fe^{2+} + 2e^- \rightarrow Fe^0 \quad E^o = -0.44\ V_{SHE}$

$Ni^{2+} + 2e^- \rightarrow Ni^0 \quad E^o = -0.20\ V_{SHE}$

$Fe^{2+} + H_2 \rightarrow Fe^0 + 2H^+$ (favored or unfavored) ?

$H^+ + 2e^- \rightarrow H_2 \quad E^o = 0\ V_{SHE}$

$Fe^{2+} + 2e^- \rightarrow Fe^0 \quad E^o = -0.44\ V_{SHE}$

$$\Delta_r G = -nF\Delta E$$

n: the number of electrons transferred
F: Faraday constant
(= electric charge of 1 mole of electrons = 96485 C/mol)
ΔE: potential difference

$$\Delta_r G = -nFE_H$$

$$\Delta_r G = \Delta_r G^0 + RT\ln Q_r \qquad Q_r = \frac{\{P\}^p\{Q\}^q\ldots}{\{A\}^a\{B\}^b\ldots}$$

$$\Rightarrow \quad E_H = E_H^0 - \frac{2.303\,RT}{nF}\log Q_r$$

$$\Rightarrow \quad E_H = E_H^0 - \frac{0.0591}{n}\log Q_r$$

$E_H°(W)$: $E_H°$ value for natural water conditions (pH 7), $[H^+] = 10^{-7}$

??? + ne^- + mH^+ → ???

$$\Rightarrow \quad E_H = E_H^0 - \frac{0.0591}{n} \log \frac{1}{[H^+]^m} \qquad - \left(\frac{0.0591}{n}\right) m \times pH$$

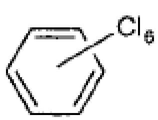
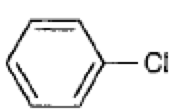
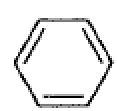
$$\Rightarrow \quad E_H = E_H^0 - \frac{(0.0591 \times 7)m}{n}$$

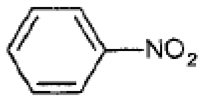
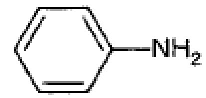
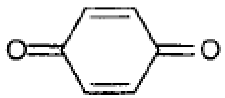
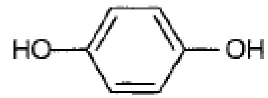
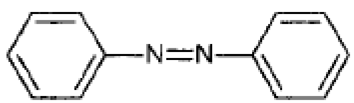
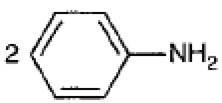
$$\Rightarrow \quad E_H = E_H^0 - \frac{0.414m}{n}$$

Table 14.2 Standard Reduction Potentials and Average Standard Free Energies of Reaction (per Electron Transferred) at 25 °C of Some Redox Couples that Are Important in Natural Redox Processes (The reactions are ordered in decreasing $E_H^0(W)$ values.) [a]

	Halfreaction: Oxidized Species = Reduced Species	E_H^0 (V)	$E_H^0(W)$ (V)	$\Delta_r G^0(W)/n^c$ ($kJ \cdot mol^{-1}$)
(1a)	$O_2(g) + 4\ H^+ + 4\ e^- = 2\ H_2O$	+1.23	+0.81	–78.3
(1b)	$O_2(aq) + 4\ H^+ + 4\ e^- = 2\ H_2O$	+1.19	+0.77	–74.3
(2)	$2\ NO_3^- + 12\ H^+ + 10\ e^- = N_2(g) + 6\ H_2O$	+1.24	+0.74	–72.1
(3)	$MnO_2(s) + HCO_3^-\ (10^{-3}) + 3\ H^+ + 2\ e^- = MnCO_3(s) + 2\ H_2O$		+0.53 [b]	–50.7 [b]
(4)	$NO_3^- + 2\ H^+ + 2\ e^- = NO_2^- + H_2O$	+0.85	+0.43	–41.6
(5)	$NO_3^- + 10\ H^+ + 8\ e^- = NH_4^+ + 3\ H_2O$	+0.88	+0.36	–35.0
(6)	$FeOOH(s) + HCO_3^-\ (10^{-3}\ M) + 2\ H^+ + e^- = FeCO_3(s) + 2\ H_2O$		–0.05 [b]	+ 4.8 [b]
(7)	CH_3COCOO^- (pyruvate) $+ 2\ H^+ + 2\ e^- = CH_3CHOHCOO^-$ (lactate)		–0.19	+17.8
(8a)	$HCO_3^- + 9\ H^+ + 8\ e^- = CH_4(aq) + 3\ H_2O$	+0.21	–0.20	+19.3
(8b)	$CO_2(g) + 8\ H^+ + 8\ e^- = CH_4(g) + 2\ H_2O$	+0.17	–0.24	+23.6
(9)	$SO_4^{2-} + 9\ H^+ + 8\ e^- = HS^- + 4\ H_2O$	+0.25	–0.22	+20.9
(10)	$S(s) + 2\ H^+ + 2\ e^- = H_2S(aq)$	+0.14	–0.27	+26.0
(11a)	$2\ H^+ + 2\ e^- = H_2(aq)$	+0.08	–0.33	+31.8
(11b)	$2\ H^+ + 2\ e^- = H_2(g)$	0.00	–0.41	+40.0
(12)	$6\ CO_2(g) + 24\ H^+ + 24\ e^- = C_6H_{12}O_6$(glucose) $+ 6\ H_2O$	–0.01	–0.43	+41.0

Table 14.3 Standard Reduction Potentials and Average Standard Free Energies of Reaction (per Electron Transferred) at 25°C of Some Organic Redox Couples in Aqueous Solution (The reactions are ordered in decreasing $E_H(W)$ values.) [a]

	Halfreaction					
	Oxidized Species		Reduced Species	E_H^0 (V)	$E_H^0(W)$ [b] (V)	$\Delta_r G^0(W)/n$ [c] ($kJ \cdot mol^{-1}$)
(1)	$CCl_3{-}CCl_3 + 2e^-$	=	$Cl_2C{=}CCl_2 + 2Cl^-$	+ 0.95	+ 1.13	- 109.0
(2)	$CBr_4 + H^+ + 2e^-$	=	$CHBr_3 + Br^-$	+ 0.89	+ 0.83	- 80.1
(3)	$CCl_4 + H^+ + 2e^-$	=	$CHCl_3 + Cl^-$	+ 0.79	+ 0.67	- 64.7
(4)	$CHBr_3 + H^+ + 2e^-$	=	$CH_2Br_2 + Br^-$	+ 0.67	+ 0.61	- 58.9
(5)	$Cl_2C{=}CCl_2 + H^+ + 2e^-$	=	$Cl_2C{=}CHCl + Cl^-$	+ 0.70	+ 0.58	- 56.0
(6)	$CHCl_3 + H^+ + 2e^-$	=	$CH_2Cl_2 + Cl^-$	+ 0.68	+ 0.56	- 54.0
(7)	 $+ H^+ + 2e^-$	=	 $+ Cl^-$	+ 0.68	+ 0.56	- 54.0
(8)	 $+ H^+ + 2e^-$	=	 $+ Cl^-$	+ 0.54	+ 0.42	- 40.5

(9)	 $+ 6H^+ + 6e^-$	=	 $+ 2H_2O$	+ 0.83	+ 0.42	- 40.5
(10)	 $+ 2H^+ + 2e^-$	=		+ 0.70	+ 0.28	- 27.0
(11)	$H_3C-S(=O)-CH_3$ $+ 2H^+ + 2e^-$	=	$H_3C-S-CH_3 + H_2O$	+ 0.57	+ 0.16	- 15.4
(12)	 $+ 4H^+ + 4e^-$	=	2 	+ 0.31	- 0.10	+ 9.7
(13)	$CH_3-S(=O)_2-CH_3$ $+ 2H^+ + 2e^-$	=	$H_3C-S(=O)-CH_3$ $+ H_2O$	+ 0.17	- 0.24	+ 23.2
(14)	$R-S-S-R$ $+ 2H^+ + 2e^-$ (cystine)	=	$2R-SH$ (cysteine)	+ 0.02	- 0.39	+ 37.6

2. One-Electron Reduction Potentials

(reduction potentials for sequential reactions)

$$BQ + H^+ + e^- \rightleftharpoons SQ; \qquad E_H^1(W) = +0.10\ V$$

$$SQ + H^+ + e^- \rightleftharpoons HQ; \qquad E_H^2(W) = +0.46\ V$$

$$BQ + 2H^+ + 2e^- \rightleftharpoons HQ \qquad E_H(W) = ???$$

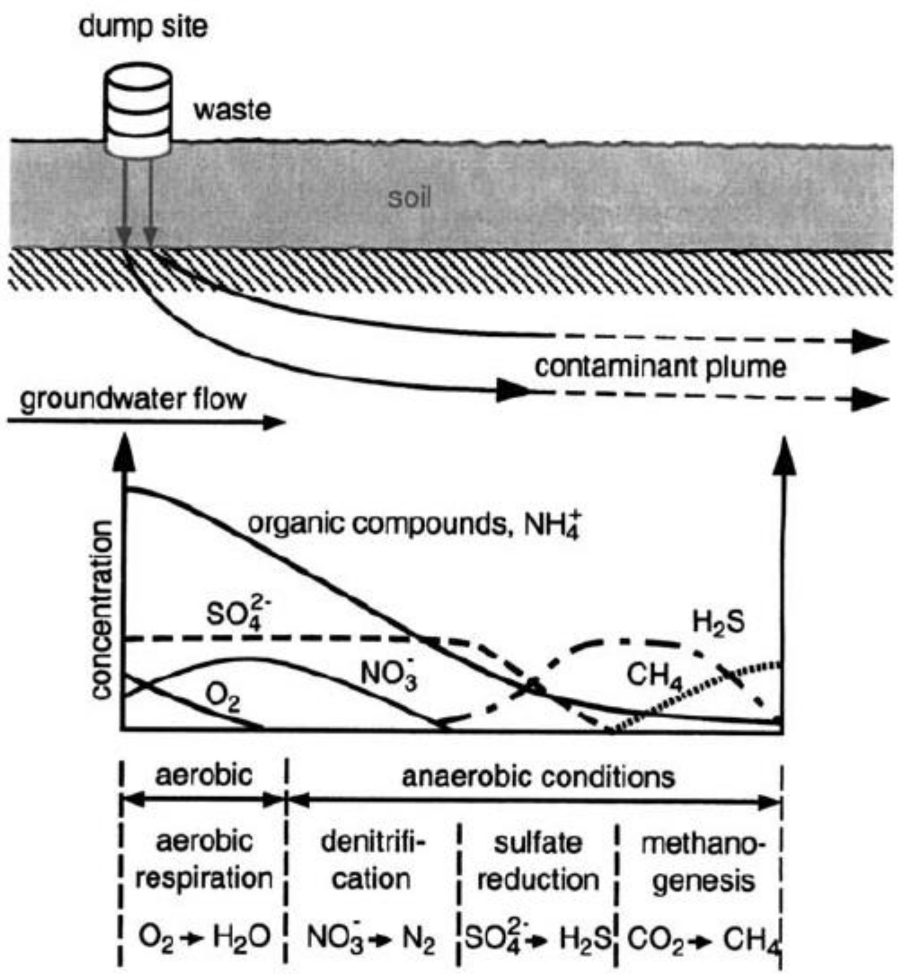
$$\Delta_r G^0 = \Delta_r G^1 + \Delta_r G^2 + \ldots + \Delta_r G^n = \sum_{k=1}^{n} \Delta_r G^k$$

$$\Rightarrow \quad E_H^0 = \frac{1}{n}\sum_{k=1}^{n} E_H^k \qquad \Delta_r G = -nF\Delta E$$

$$\Rightarrow \quad E_H^0(W) = \frac{1}{n}\sum_{k=1}^{n} E_H^k(W)$$

3. Processes Determining the Redox Conditions in the Environment

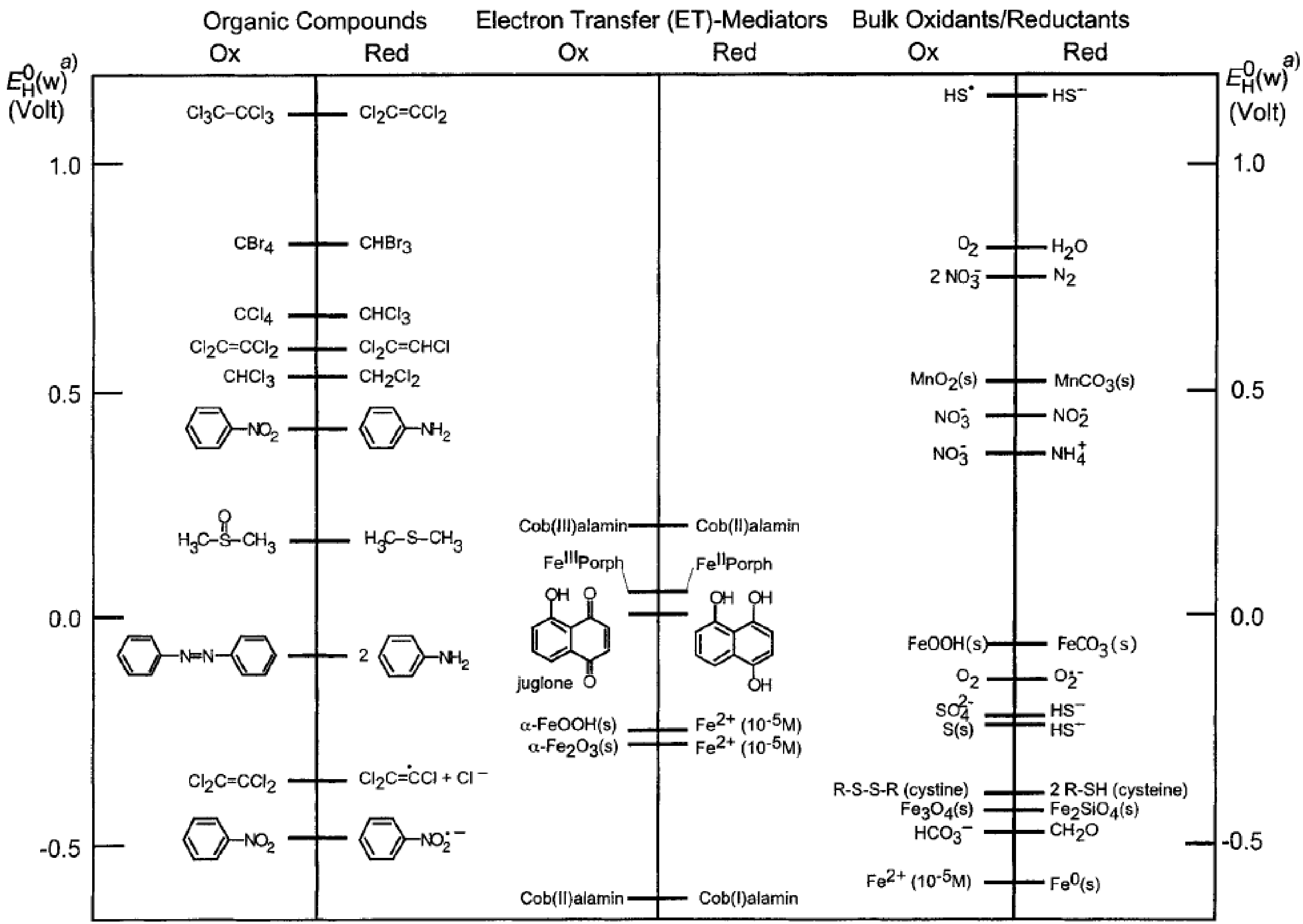
$$\frac{1}{4}CO_2(g) + \frac{1}{4}H_2O \rightleftharpoons \frac{1}{24}C_6H_{12}O_6 + \frac{1}{4}O_2(g)$$



√Electron acceptors

√ Electron donors

4. Evaluating the Thermodynamics of Redox Reactions under Environmental Conditions



a) pH = 7; $[HCO_3^-] = [Cl^-] = 10^{-3}$ M; $[Br^-] = 10^{-5}$ M

14.3 Reaction Pathways and Kinetics of Redox Reactions

1. Factors Determining the Rate of Redox Reactions

Compound + Oxidant (or Reductant) $\rightarrow$ Products

C O R

$$d[C]/dt = f(\ ?\ )$$

$$d[C]/dt = -k[C][O]$$

- Concentrations of C, O, P
- Temperature, pH
- Water constituents: NOM, inorganic ions, oxygen, & others

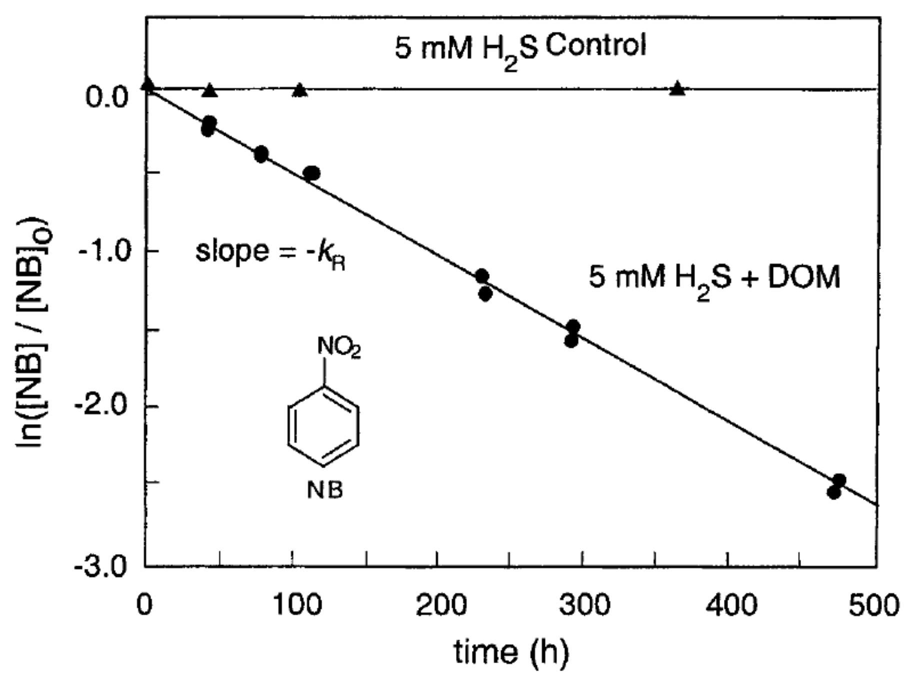
2. Reduction of Nitroaromatic Compounds (NACs)

√ NACs are present as pesticides, dyes & explosives (e.g., TNT)

√ Reduction mechanism

$$\underset{\text{I}}{ArNO_2} \xrightarrow[-H_2O]{+2e^- + 2H^+} \underset{\text{II}}{ArNO} \xrightarrow{+2e^- + 2H^+} \underset{\text{III}}{ArNHOH} \xrightarrow[-H_2O]{+2e^- + 2H^+} \underset{\text{IV}}{ArNH_2}$$

√ DOM enhances the reduction rate.



$$ArNO_2 + HS^- + H^+ \rightarrow ArNO + S_{(s)} + H_2O$$

Two-electron transfer reaction

Half reactions:

$$ArNO_2 + 2H^+ + 2e^- \rightarrow ArNO + H_2O \qquad E^o = +0.75\ V_{SHE}$$

$$S_{(s)} + H^+ + 2e^- \rightarrow HS^- \qquad E^o = -0.25\ V_{SHE}$$

Favored or Unfavored

What if the actual reaction proceeds by two single electron transfer mechanism

$$ArNO_2 + HS^- \rightarrow ArNO_2^{\bullet -} + HS^{\bullet} \qquad (1)$$

$$ArNO_2^{\bullet -} + HS^{\bullet} + H^+ \rightarrow ArNO + S_{(s)} + H_2O \qquad (2)$$

$$ArNO_2 + HS^- \rightarrow ArNO_2^{\bullet -} + HS^\bullet \qquad (1)$$

Half reactions:

$$ArNO_2 + e^- \rightarrow ArNO_2^{\bullet -} \qquad E^o = -0.5\ V_{SHE}$$

$$HS^\bullet + e^- \rightarrow HS^- \qquad E^o = +1.1\ V_{SHE}$$

Favored or Unfavored

$$ArNO_2^{\bullet -} + HS^\bullet + H^+ \rightarrow ArNO + S_{(s)} + H_2O \qquad (2)$$

Half reactions:

$$ArNO_2^{\bullet -} + 2H^+ + e^- \rightarrow ArNO + H_2O \qquad E^o = +2\ V_{SHE}$$

$$S_{(s)} + H^+ + e^- \rightarrow HS^\bullet \qquad E^o = -1.6\ V_{SHE}$$

Favored or Unfavored

In the presence of DOM,

$$DOM + HS^{-} \rightarrow DOM_{red} + HS^{\bullet} \quad (1)$$

$$ArNO_2 + DOM_{red} \rightarrow ArNO_2^{\bullet -} + DOM \quad (2)$$

$$ArNO_2^{\bullet -} + HS^{\bullet} + H^{+} \rightarrow ArNO + S_{(s)} + H_2O \quad (3)$$

$$DOM + HS^{-} \rightarrow DOM_{red} + HS^{\bullet} \quad (1)$$

Half reactions:

$$DOM + e^{-} \rightarrow DOM_{red} \qquad E^{o} = -0.4 \sim +0.5\ V_{SHE}$$

$$HS^{\bullet} + e^{-} \rightarrow HS^{-} \qquad E^{o} = +1.1\ V_{SHE}$$

Favored or Unfavored

$$ArNO_2 + DOM_{red} \rightarrow ArNO_2^{\bullet -} + DOM \qquad (2)$$

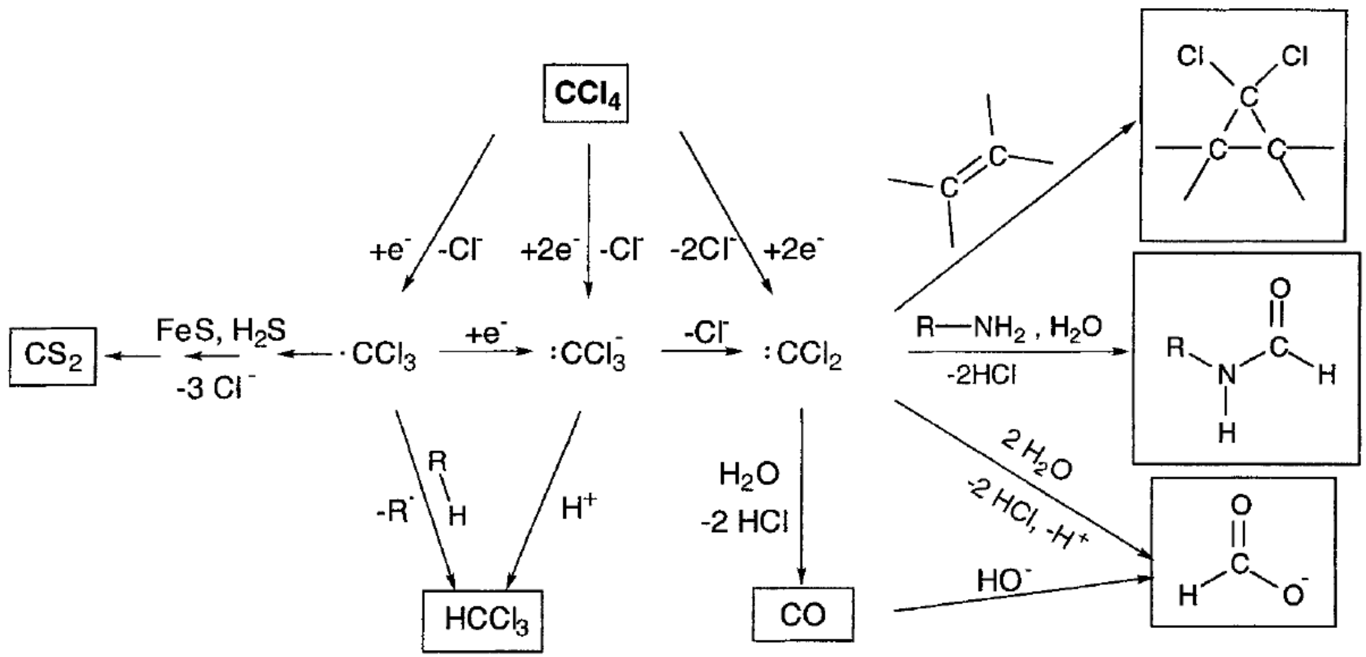
Half reactions:

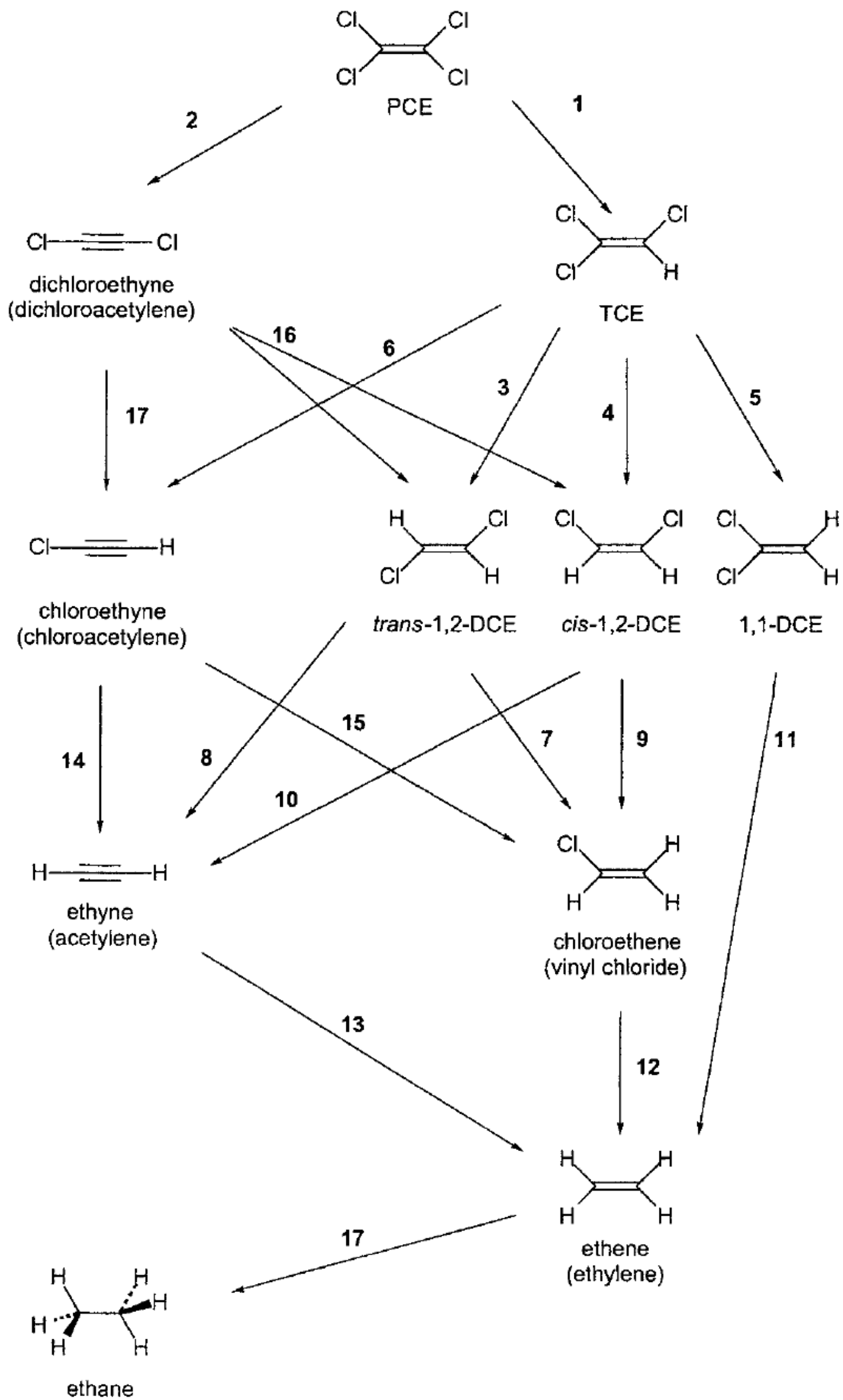
$$ArNO_2 + e^- \rightarrow ArNO_2^{\bullet -} \qquad E^o = -0.5\ V_{SHE}$$

$$DOM + e^- \rightarrow DOM_{red} \qquad E^o = -0.4 \sim +0.5\ V_{SHE}$$

Favored or Unfavored

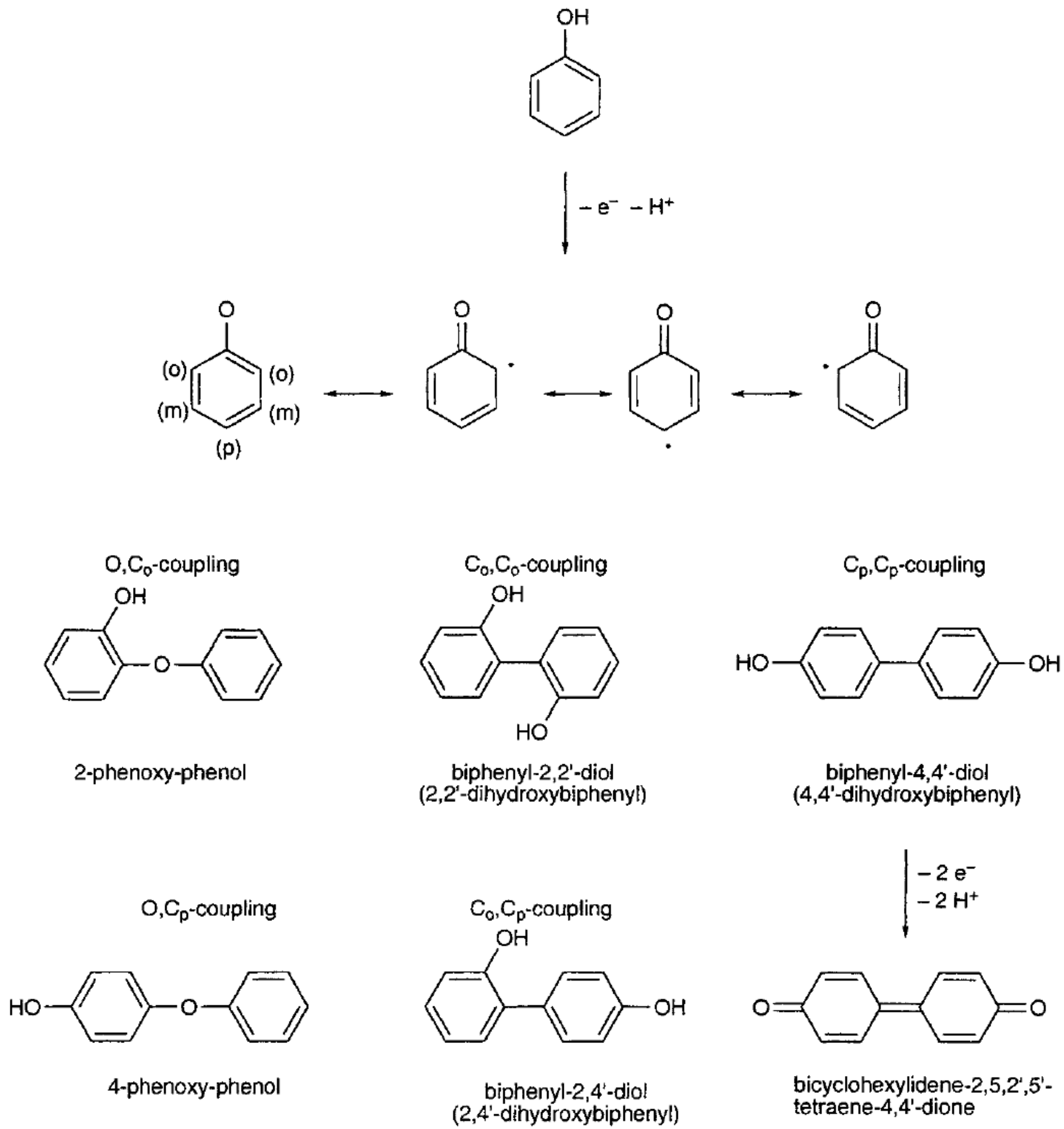
3. Reductive Dehalogenation Reactions of Polyhalogenated C_1- and C_2-Compounds

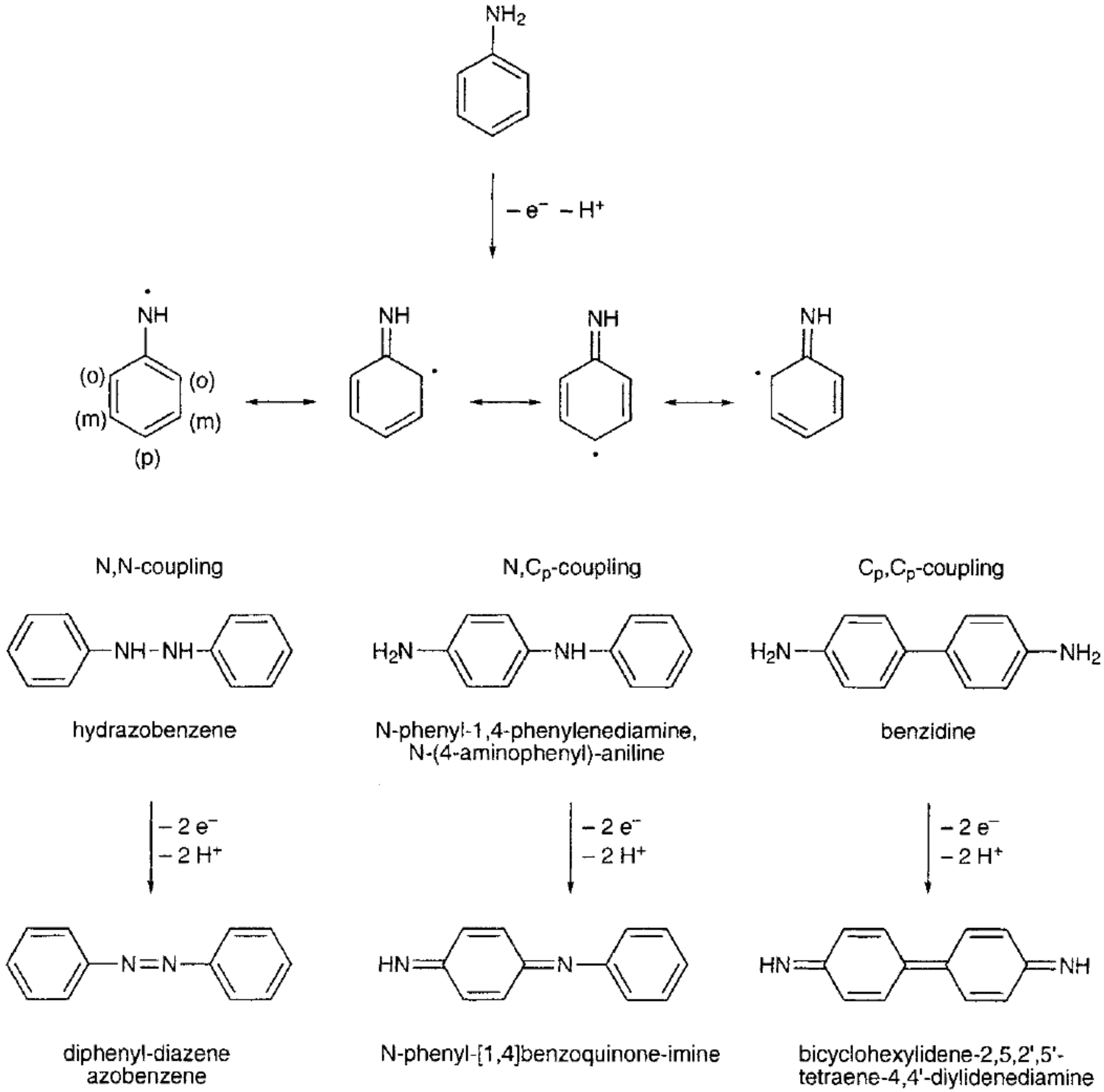




Cl
Cl
Cl
Cl
PCE
1
2
dichloroethyne
(dichloroacetylene)
TCE
16
6
3
4
5
17
chloroethyne
(chloroacetylene)
trans-1,2-DCE
cis-1,2-DCE
1,1-DCE
14
8
15
7
9
11
10
ethyne
(acetylene)
chloroethene
(vinyl chloride)
13
12
17
ethene
(ethylene)
ethane

4. Oxidation Reactions




NH2
– e⁻ – H⁺
NH
(o)
(o)
(m)
(m)
(p)
NH
NH
NH
N,N-coupling
N,Cp-coupling
Cp,Cp-coupling
NH–NH
H2N
NH
H2N
NH2
hydrazobenzene
N-phenyl-1,4-phenylenediamine,
N-(4-aminophenyl)-aniline
benzidine
– 2 e⁻
– 2 H⁺
– 2 e⁻
– 2 H⁺
– 2 e⁻
– 2 H⁺
N=N
HN
N
HN
NH
diphenyl-diazene
azobenzene
N-phenyl-[1,4]benzoquinone-imine
bicyclohexylidene-2,5,2',5'-
tetraene-4,4'-diylidenediamine

Chapter 15

Direct Photolysis

15.1 Introduction

√ Direct photolysis vs. Indirect photolysis

√ Primary photo-processes

$$A + h\nu \rightarrow A^* \quad \text{(photo-excitation)}$$

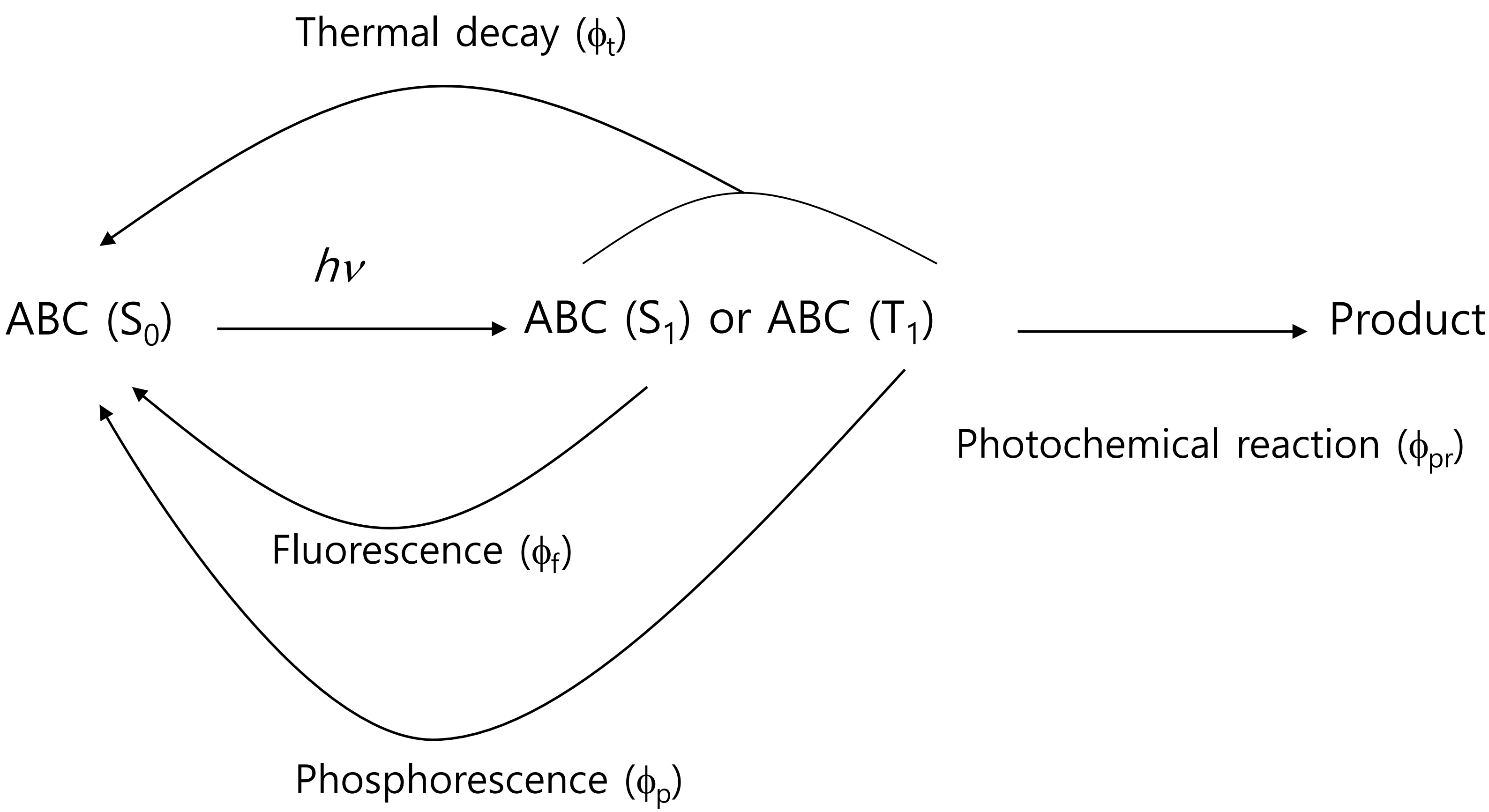
$$A^* \rightarrow A + \text{heat} \quad \text{(thermal decay)}$$

$$A^* \rightarrow A + h\nu' \quad \text{(fluorescence)}$$

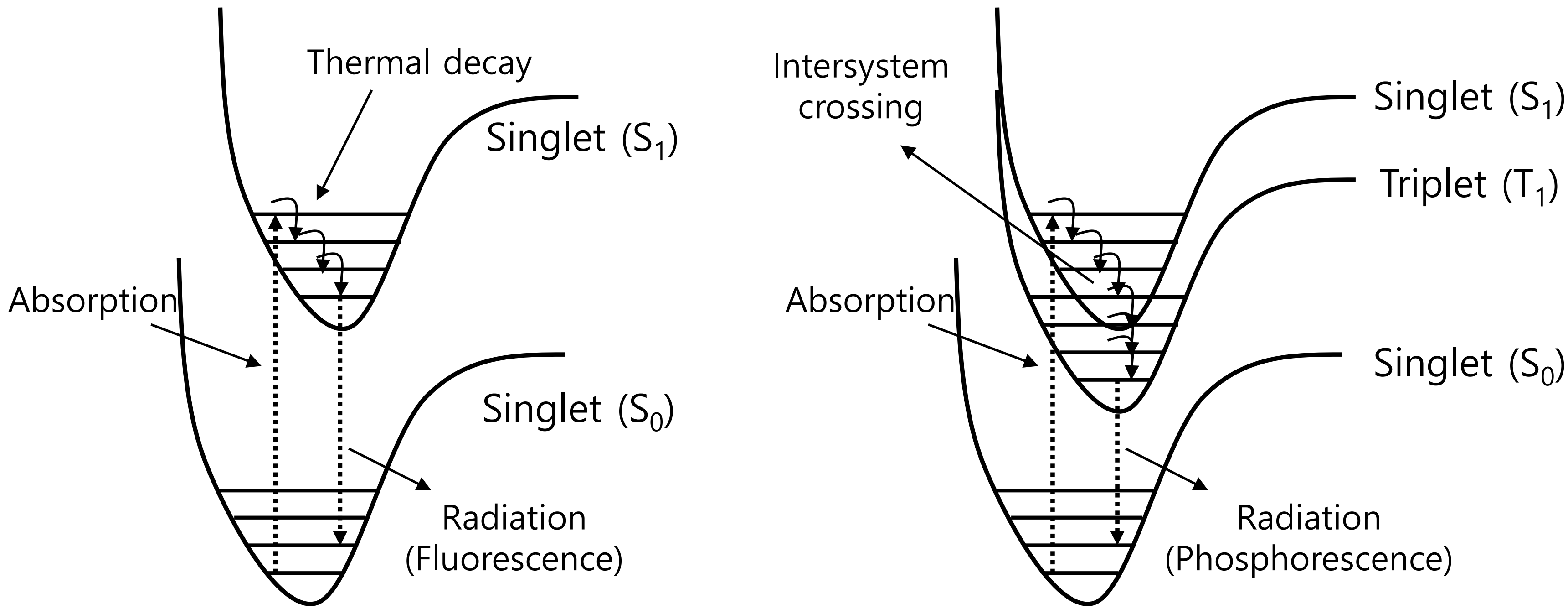
$$A^* \rightarrow A + h\nu'' \quad \text{(phosphorescence)}$$

$$A^* \rightarrow B \quad \text{((direct) photolysis)}$$

◆ Primary Photo-Processes



◆ Fluorescence and Phosphorescence

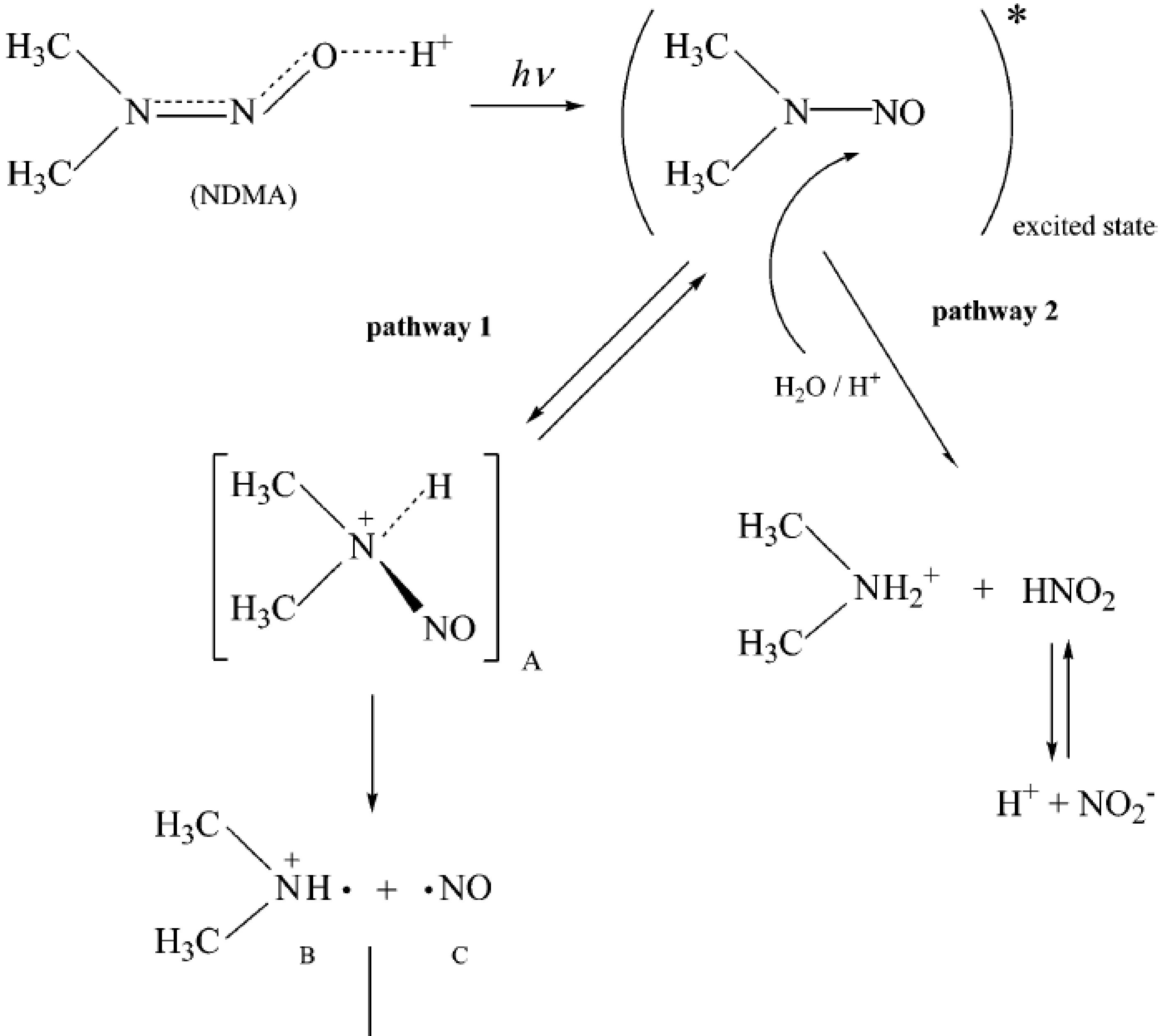


Fluorescence

Phosphorescence

◆ Photochemical Reactions

ABC (S_1) or ABC (T_1)	$\Rightarrow AB\cdot + C\cdot$	Dissociation into radicals
	$\Rightarrow E + F$	Intramolecular decompositio n into molecules
	$\Rightarrow ACB$	Intramolecular rearrangement
	$\Rightarrow ABC'(S_1)$ or $ABC'(T_1) \Rightarrow ABC'(S_0)$	Photoisomerization
	$+ RH \Rightarrow ABCH\cdot + R\cdot$	Hydrogen-atom abstract
	$+ ABC \Rightarrow (ABC)_2$	Photodimerization
	$+ D \Rightarrow ABC + \text{product}$	Photosensitized reaction
	$\Rightarrow ABC^+ + e^-$	Photoionization
	$+ D \Rightarrow ABC^{+(or-)} + D^{-(or+)}$	"External" electron transfer
	$\Rightarrow AB^+ + C^-$	"Internal" electron transfer

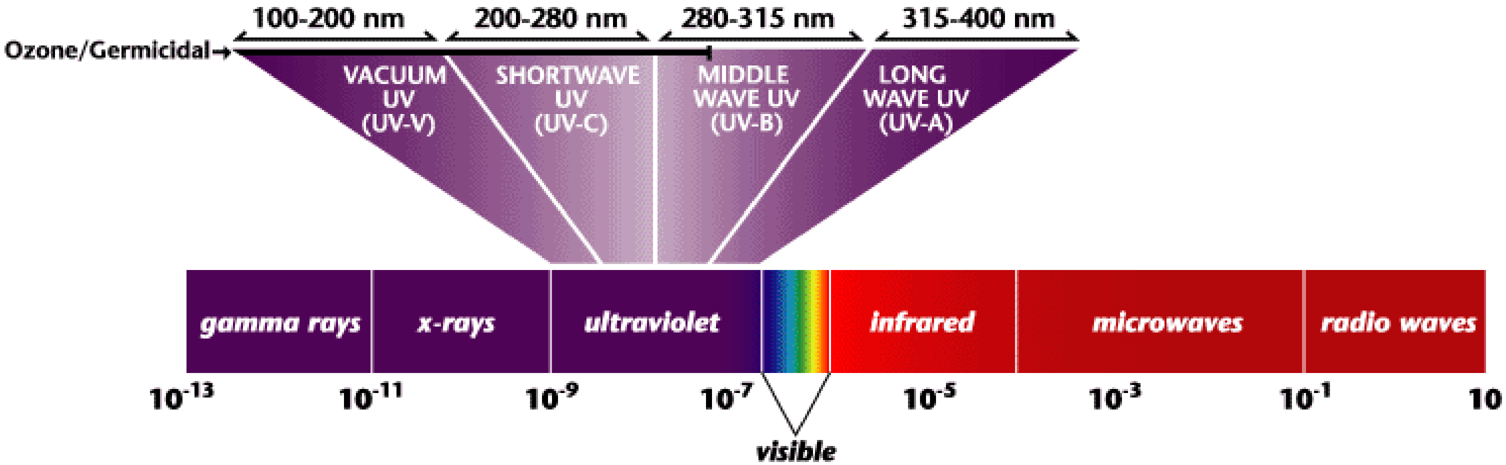


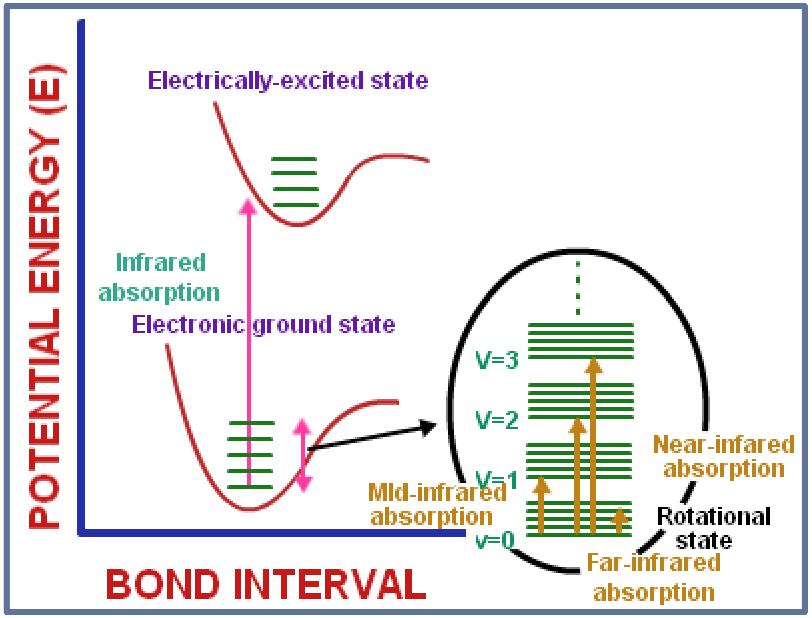
Lee et al., 2005 (*Environ. Sci. Technol.*)

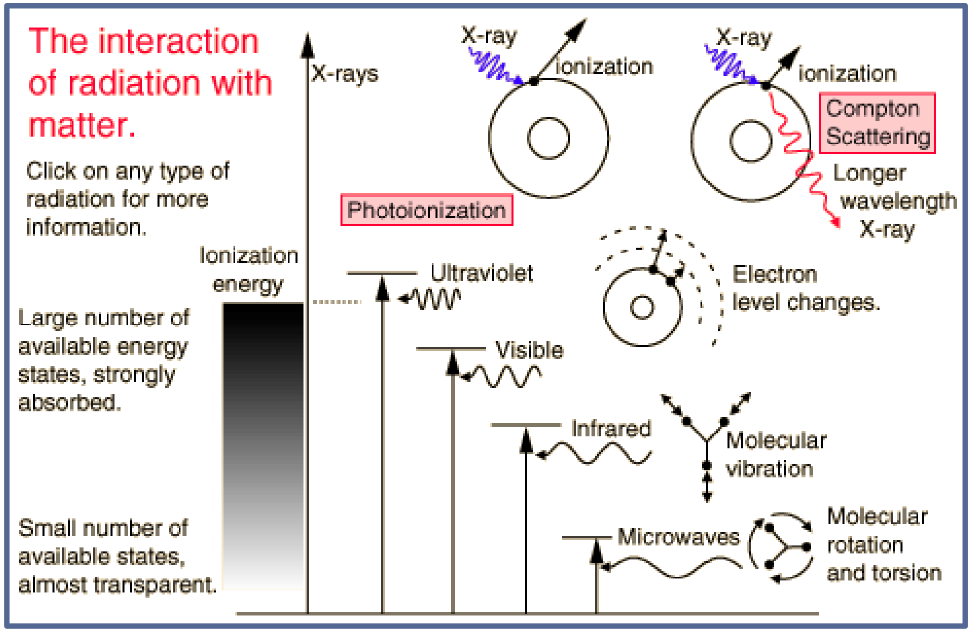
15.2 Some Basic Principles of Photochemistry

1. Light Absorption by Chemical Species: Molar Extinction Coefficients

√ Electromagnetic Spectrum







√ Planck Law of Radiation

$$\mathbf{u = \mathit{hv} = \mathit{h}c/\lambda}$$

$$\mathbf{U = N_A \mathit{hv} = \mathit{h}cN_A/\lambda}$$

Where u = energy (J) of one photon
v = frequency (s^{-1})
λ = wavelengh (m)
c = speed of light (2.9979x0^{8} ms^{-1})
h = Planck constant (6.6261x10^{-34} Js)
N_A = Avogadro number (6.02214 x10^{23} mol^{-1})
U = energy per Einstein

√ Photon energy

Range Name	Wavelength Range / nm	Energy Range (kJ einstein^{-1})
Near Infrared	700 – 1000	120 – 171
Visible	400 – 700	171 – 299
Ultraviolet		
UVA	315 – 400	299 – 380
UVB	280 – 315	380 – 427
UVC	200 – 280	427 – 598
Vacuum Ultraviolet (VUV)	100 – 200	598 – 1196

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.

√ Beer-Lambert absorption law

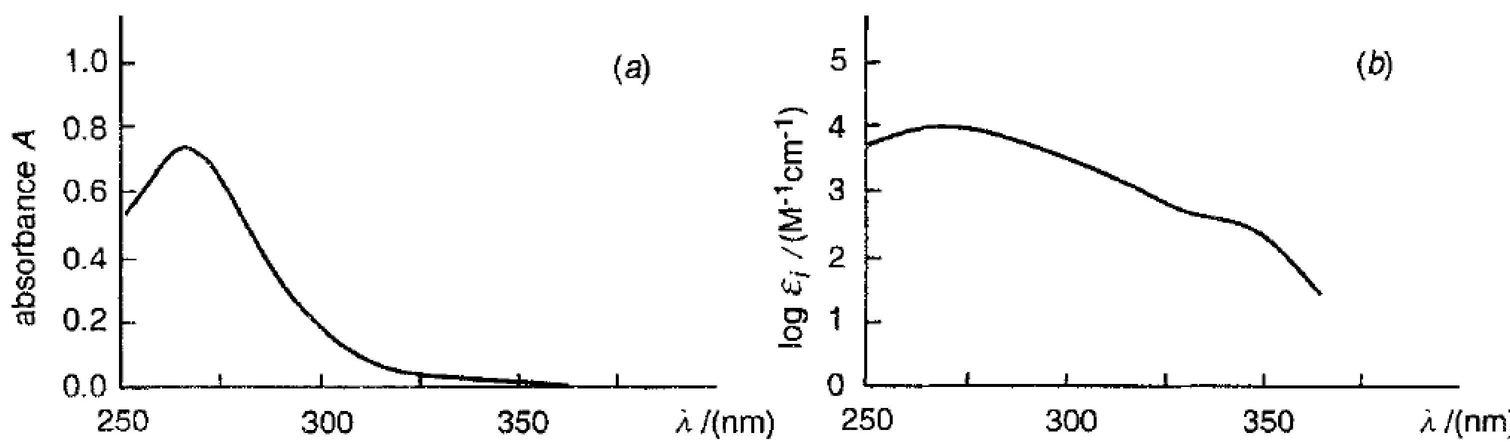
$$A = \log I_o/I = \varepsilon bC$$

$$I / I_0 = 10^{-\varepsilon bC}$$

Functions of wavelength

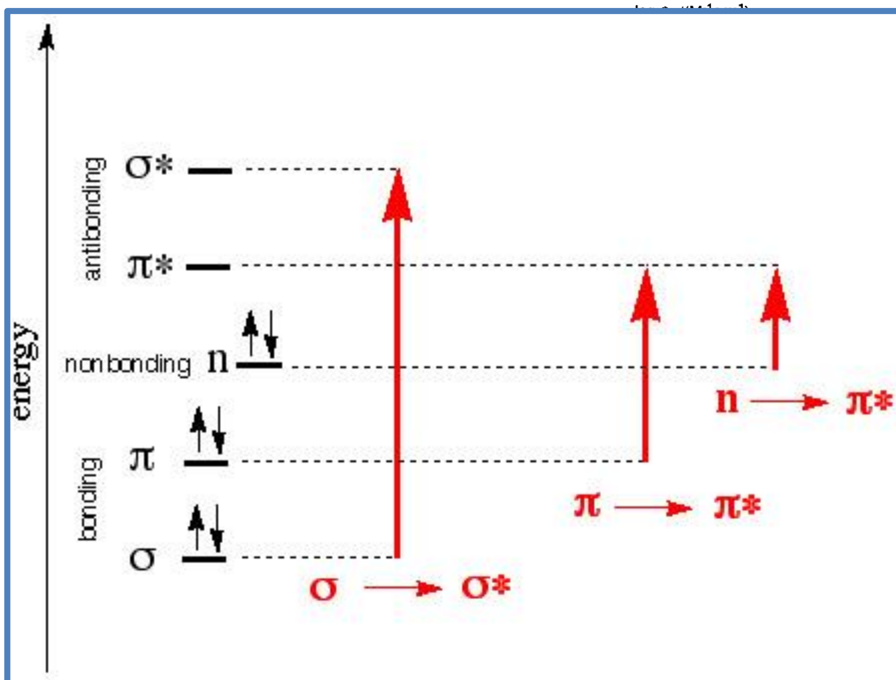
$$A = A(\lambda)$$
$$I = I(\lambda)$$
$$\varepsilon = \varepsilon(\lambda)$$

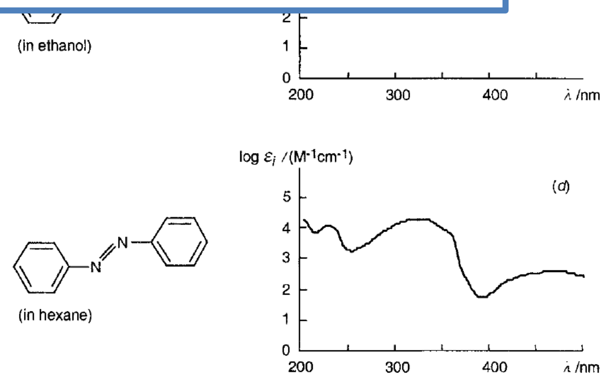
ε: molar aborption coefficient (M^{-1} cm^{-1})
b: optical pathlength (cm)
C: molar concentration of photon absorber (M)

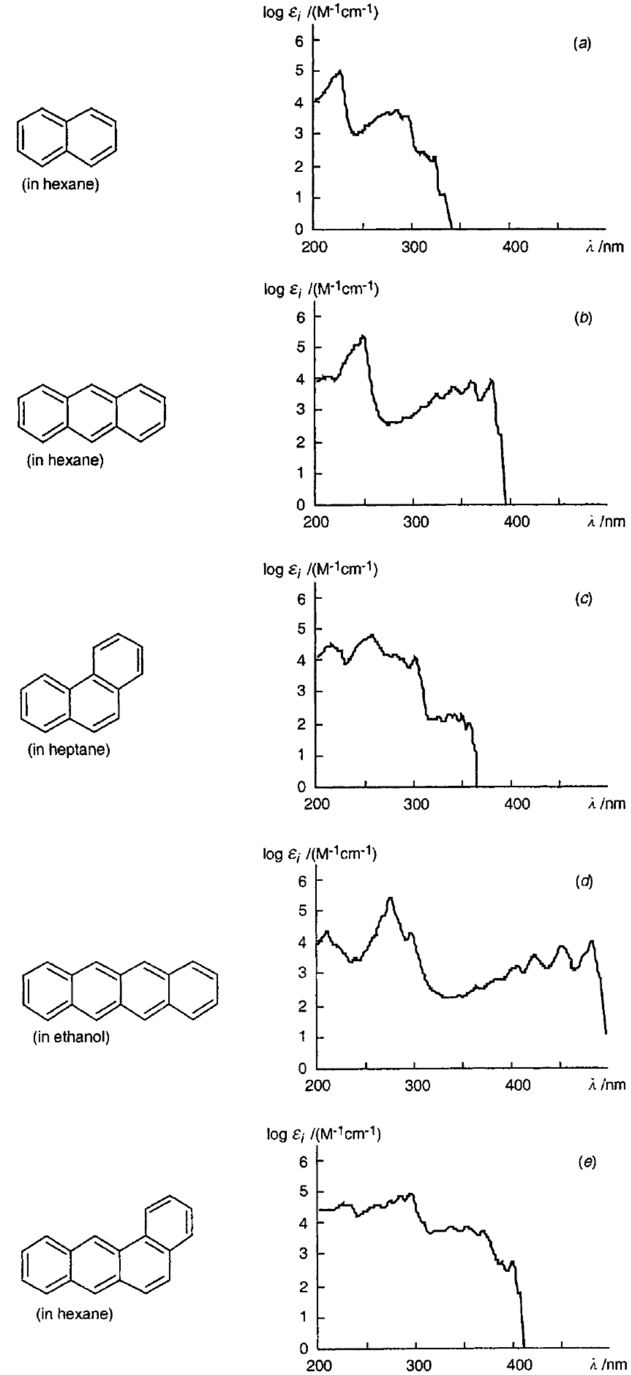


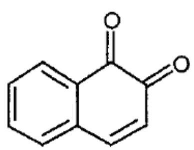
2. Chemical Structure and Light Absorption

- n → π*, π → π* transition
- More conjugated double bonds & aromatic rings shift the absorption peaks to longer wavelength ranges

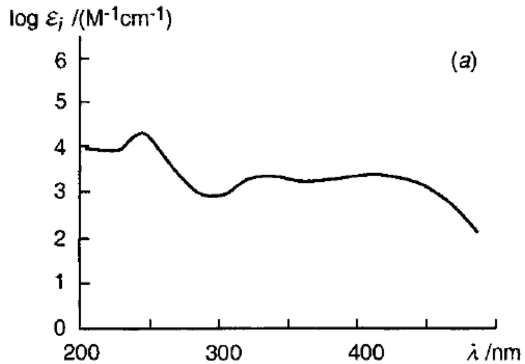


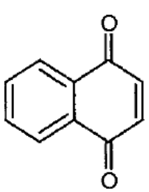




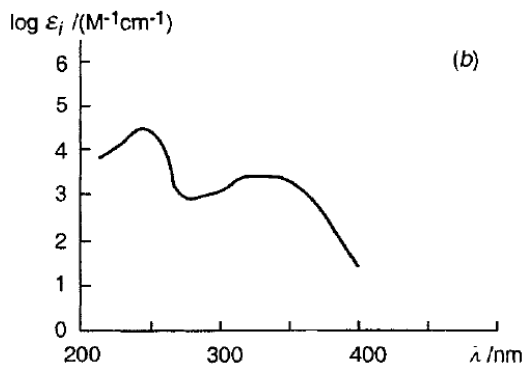


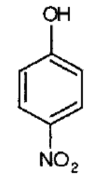
(in methanol)



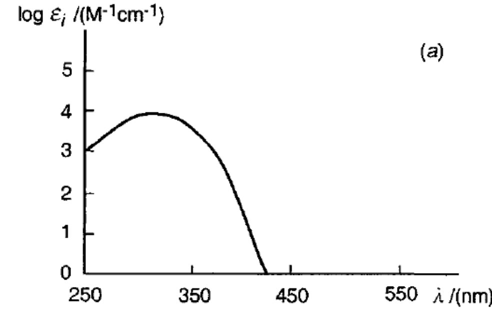


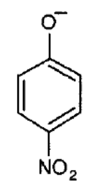
(in methanol)



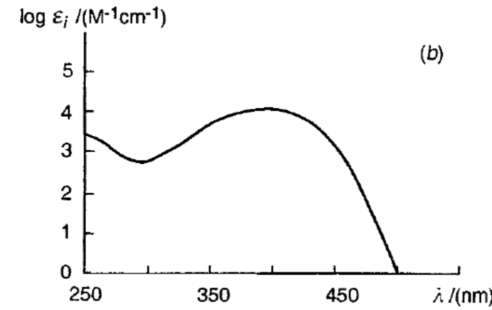


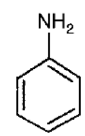
(in water)



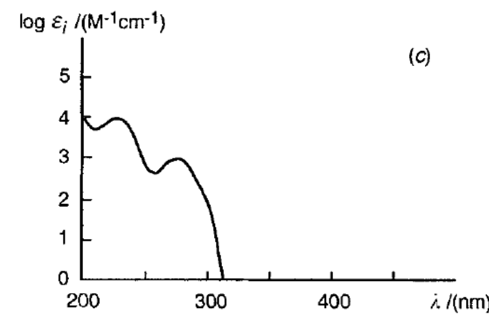


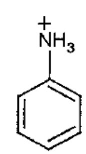
(in water)



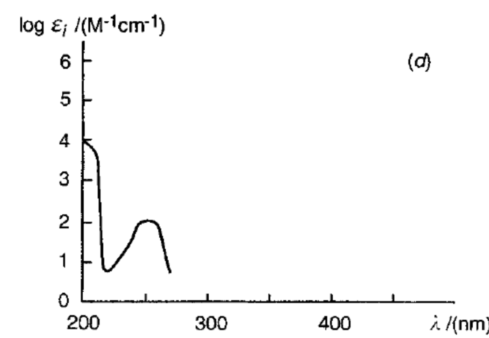


(in water)





(in water)



3. The Fate of Excited Chemical Species: Quantum Yields

√ Definition

$$A + h\nu \rightarrow B$$

$$\phi_A = \frac{\text{Molecules (mole) of A decomposed per unit volume per unit time}}{\text{Quanta of light (Einstein) absorbed by A per unit volume per unit time}}$$

$$\phi_B = \frac{\text{Molecules (mole) of B formed per unit volume per unit time}}{\text{Quanta of light (Einstein) absorbed by A per unit volume per unit time}}$$

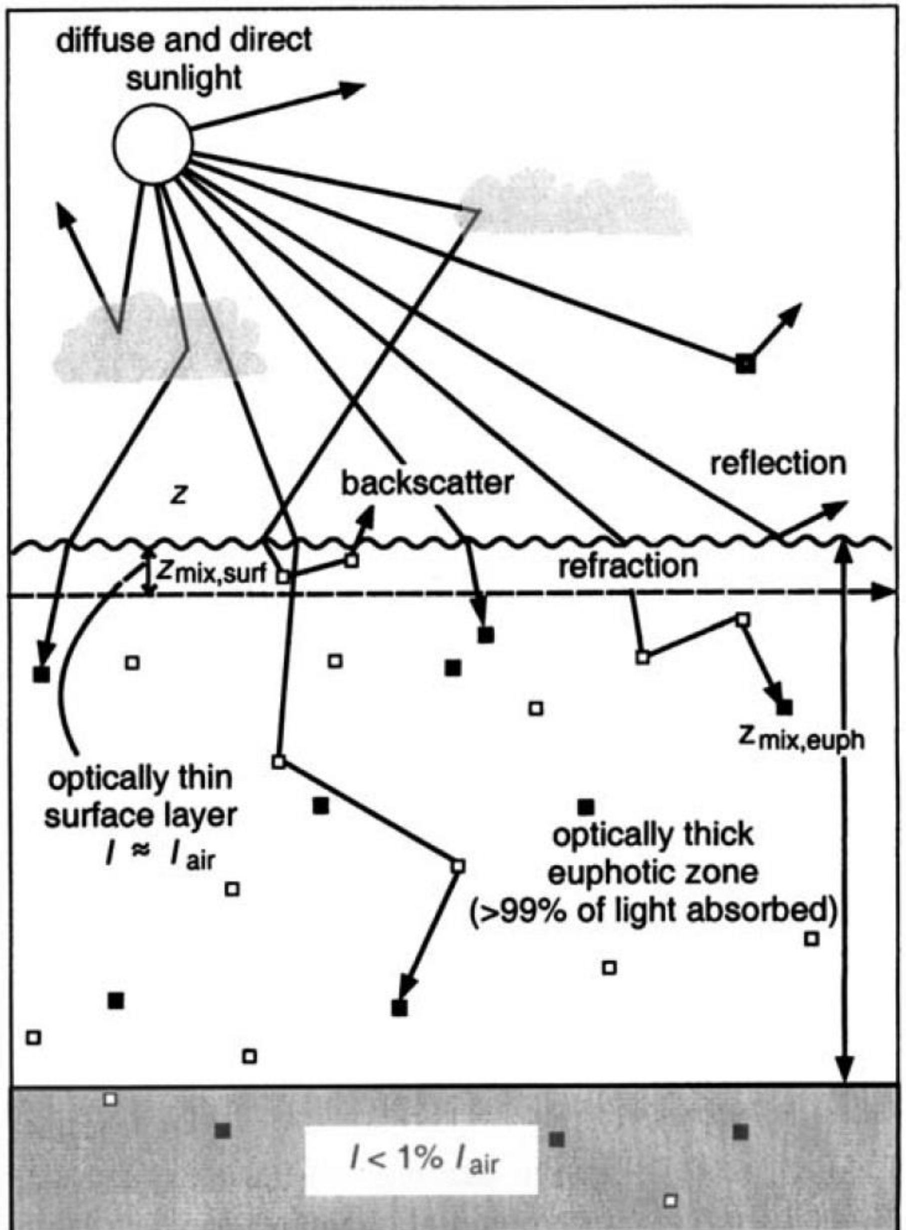
- ϕ_A is not always same as ϕ_B

√ Primary quantum yield: quantum yield for the primary photochemical reaction
√ Overall quantum yield: quantum yield considering the primary photochemical reaction and subsequent thermal reactions

Ex) $A + h\nu \rightarrow B + C$ (primary quantum yield = 0.5)
$A + C \rightarrow B$

Overall quantum yield for the photochemical production of B = 0.5 X 2 =1.0

15.3 Light Absorption by Organic Compounds in Natural Waters



15.4 Quantum Yield and Rate of Direct Photolysis

1. First-Order Rate Constant for Quantification of Direct Photolysis

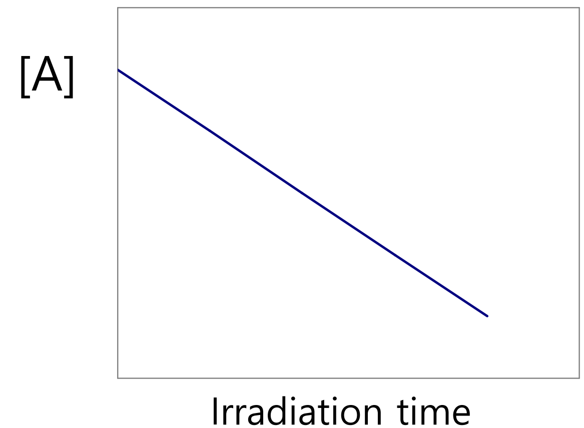
$$A + h\nu \rightarrow B$$

$$d[A]/dt = -I_A \times \phi_A = -I_0(1-10^{-\varepsilon b[A]}) \times \phi_A$$

At a high concentration ($\varepsilon bc >> 1$)

$$d[A]/dt = -I_0(1-10^{-\varepsilon b[A]}) \times \phi \approx -I_0\phi$$

Zero order kinetics



At a low concentration ($\varepsilon bc << 0.1$)

$$d[A]/dt = -I_0(1-10^{-\varepsilon b[A]}) \times \phi \approx -2.303\ I_0\varepsilon b\phi[A]$$

First order kinetics

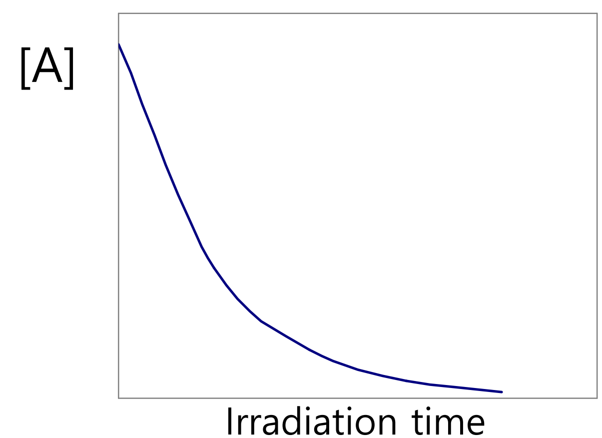


Table 15.7 Direct Photolysis Reaction Quantum Yields of Some Selected Organic Pollutants in Aqueous Solution

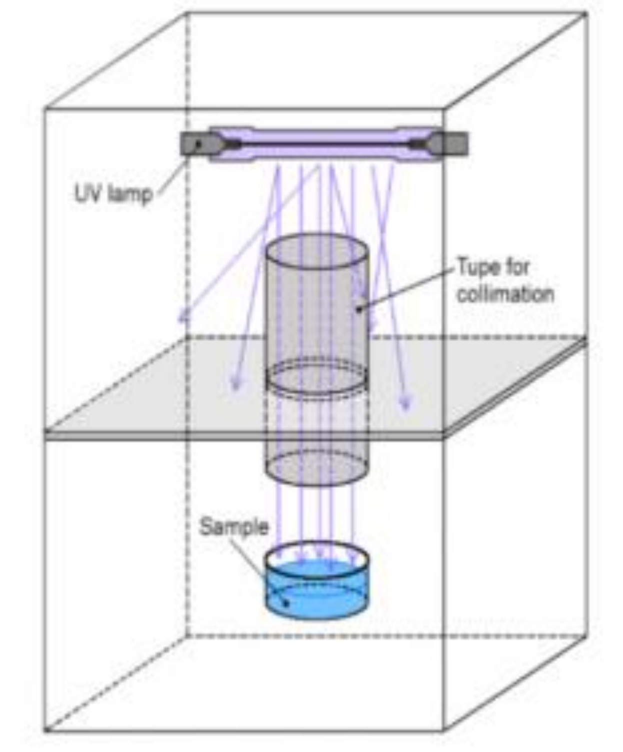
Compound	Wavelength [a] (nm)	Solvent Other Than Water [b] (pH)	Reaction Quantum Yield (Φ_{ir}) [c]	Ref [d]
Naphthalene	313		1.5×10^{-2}	1
1-Methylnaphthalene	313		1.8×10^{-2}	1
2-Methylnaphthalene	313		5.3×10^{-3}	1
Phenanthrene	313		1.0×10^{-2}	1
Anthracene	313		3.0×10^{-3}	1
Pyrene	313,366		2.1×10^{-3}	1
1,2-Benzanthracene	313,366,sun	1 % AN	3.2×10^{-3}	2
Benzo(a)pyrene	313,366,sun	1–20 % AN	8.9×10^{-4}	2
3,4-Dichloroaniline	313,polychr.	pH 7–10	4.4×10^{-2}	3
3,5-Dichloroaniline	313,sun	pH 4–10	5.2×10^{-2}	3
Pentachlorophenolate	314,polychr.	pH 8–10	1.3×10^{-2}	3
4-Nitrophenol	313,polychr.	pH 2–4	1.1×10^{-4}	3
4-Nitrophenolate	365,polychr.	pH 9–10	8.1×10^{-6}	3
Nitrobenzene	313		2.9×10^{-5}	4
4-Nitrotoluene	366		5.2×10^{-3}	4
2,4-Dinitrotoluene	313		2.0×10^{-3}	4
2,4,6-Trinitrotoluene	313,366,sun		2.1×10^{-3}	5

2. Determination of Quantum Yields and Chemical Actinometry

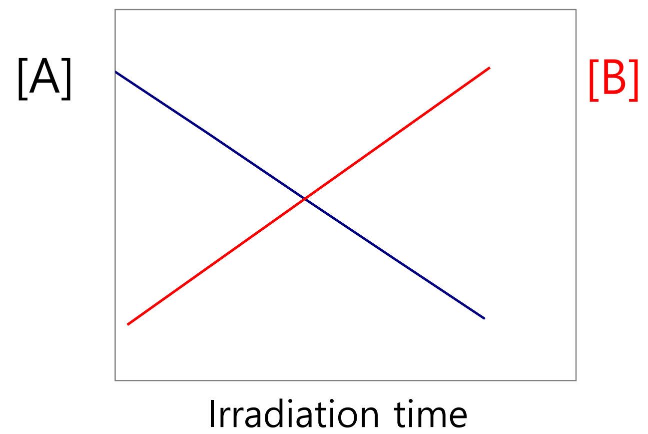
√ Determination of ϕ

$$A + h\nu \rightarrow B$$

-We need a “Collimated beam reactor” and a radiometer to determine I_0



At a high concentration of A



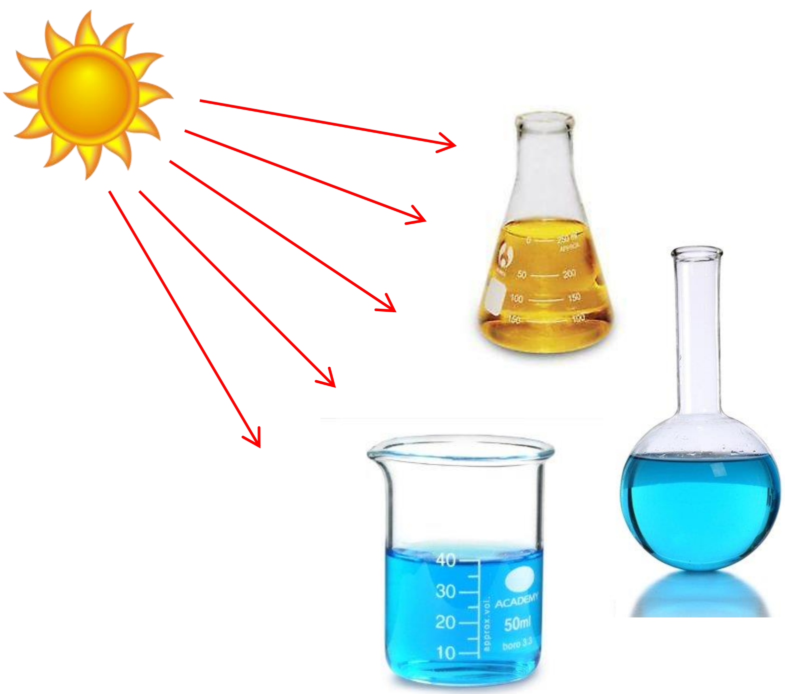
$$-d[A]/dt = d[B]/dt$$
$$= I_0 \times \phi \text{ (slope)}$$

$$\phi = \text{Slope}/I_0$$

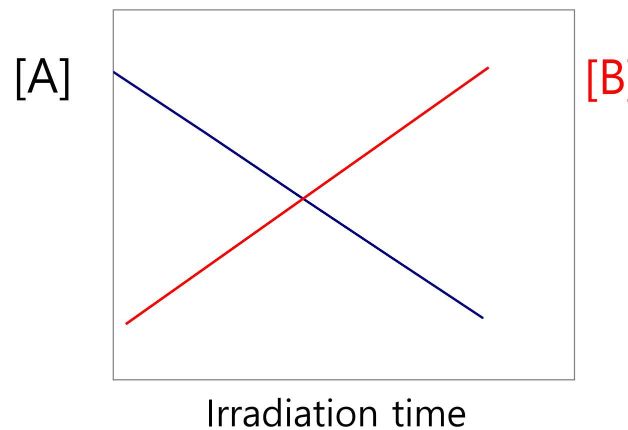
√ Chemical actinometry: a method to determine the incident light intensity (I_0, Enistein/L/s) using a chemical called a "chemical actinometer" of which ϕ is already known

$$A + h\nu \rightarrow B$$

Any shapes of reactors or systems



At a high concentration of A



$$-d[A]/dt = d[B]/dt$$
$$= I_0 \times \phi \text{ (slope)}$$

$$I_0 = \text{Slope}/\phi$$

15.5 Effects of Solid Sorbents (Particles, Soil Surfaces) on Direct Photolysis

1. Effect of Particles in Water

√ Negative effect: light-shielding effects (light absorption and scattering by particles)

√ Positive effect: surface-catalyzed reaction (photo-catalytic reactions)

2. Direct Photolysis on Soil Surfaces

√ Heterogeneous solution:

-Different from the photolysis of homogeneous solution (Adsorption + Photolysis)

-Different kinetic models are required (it's difficult to develop good ones because of the complexity of heterogeneous systems)

오염물질의 광분해(Photolysis)

➢ 직접 광분해(Direct photolysis)

$$T + h\nu \rightarrow P$$

T: Target compound
P: Product

➢ 간접 광분해(Indirect photolysis)

$$A + h\nu \rightarrow R$$
$$R + T \rightarrow P$$

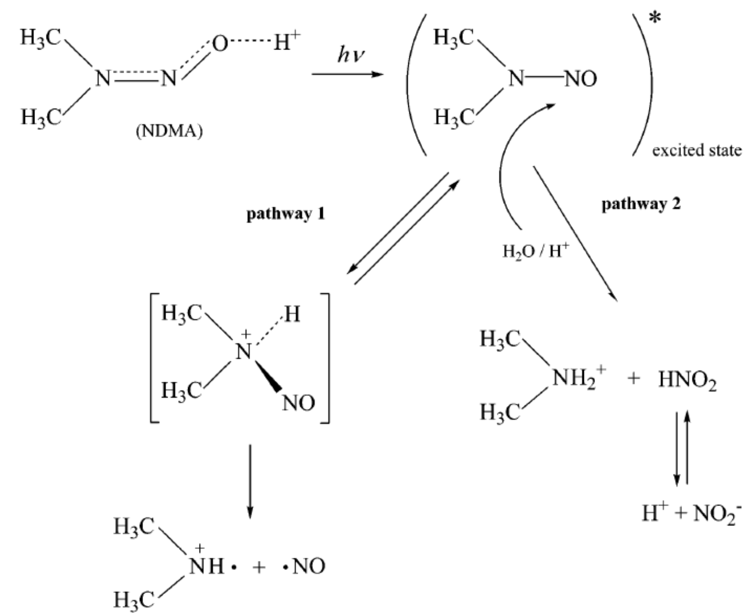
A: Light absorbing compound
R: Reactive species

➢ 광촉매반응(photo-catalysis)

$$C + h\nu \rightarrow R$$
$$R + T \rightarrow C + P$$

C: Photo-catalyst

e.g. NDMA photolysis



e.g. UV/H_2O_2 system

$$H_2O_2 + h\nu \rightarrow 2{\cdot}OH$$
$$\text{Compounds} + {\cdot}OH \rightarrow \text{Products}$$

e.g. TiO_2 photo-catalysis

$$TiO_2 + h\nu \rightarrow TiO_2(h^+ \,\&\, e^-)$$
$$\text{Compounds} + TiO_2(h^+ \,\&\, e^-) \rightarrow \text{Products} + TiO_2$$

Chapter 16

Indirect Photolysis: Reactions with Photooxidants in Natural Waters and in the Atmosphere

16.1 Introduction

√ Indirect photolysis

$$A + h\nu \rightarrow \text{Reactive species (usually oxidants)}$$
$$\text{Reactive species + Compound} \rightarrow \text{Products}$$

Oxidants: $^{\bullet}OH$, O_3, $^1O_2$, $HO_2^{\bullet}$($O_2^{\bullet-}$) (ROS: Reactive Oxygen Species)
Organo radical($R^{\bullet}$), Organoperoxyl radical($ROO^{\bullet}$)…
$CO_3^{\bullet-}$, $NO_2^{\bullet}$, $SO_4^{\bullet-}$… (Inorganic radicals)

Table 16.1 Standard One-Electron Reaction Potentials, E_H^1, in Aqueous Solution at 25°C of Some Environmentally and Technically Important (Photo)Oxidants [a]

Oxidant	Reaction in Water	E_H^1 / V
$HO^\bullet$	$HO^\bullet + e^- = HO^-$	1.9
O_3	$O_3^\bullet + e^- = O_3^-$	1.0
$^1O_2$	$^1O_2 + e^- = O_2^{\bullet-}$	0.83
$HO_2^\bullet / O_2^{\bullet-}$	$HO_2^\bullet + e^- = HO_2^-$	0.75
$^3O_2$	$^3O_2 + e^- = O_2^{\bullet-}$	–0.16
$ArO^\bullet$ [b]	$ArO^\bullet + e^- = ArO^-$	0.79
R,X–$ArO^\bullet$ [b]	R,X–$ArO^\bullet + e^-$ = R,X–ArO^-	0.2 – 1.2
$RO^\bullet$ [c]	$RO^\bullet + e^- = RO^-$	1.2
$ROO^\bullet$ [c]	$ROO^\bullet + e^- = ROO^-$	0.77
$CO_3^{\bullet-}$	$CO_3^{\bullet-} + e^- = CO_3^{2-}$	1.6
$NO_3^\bullet$	$NO_3^\bullet + e^- = NO_3^-$	2.3

[a] Data from Sulzberger et al. (1997) and Faust (1999). E_H^1 values of additional species can be found in Faust (1999). [b] Ar = phenyl. [c] R = alkyl.

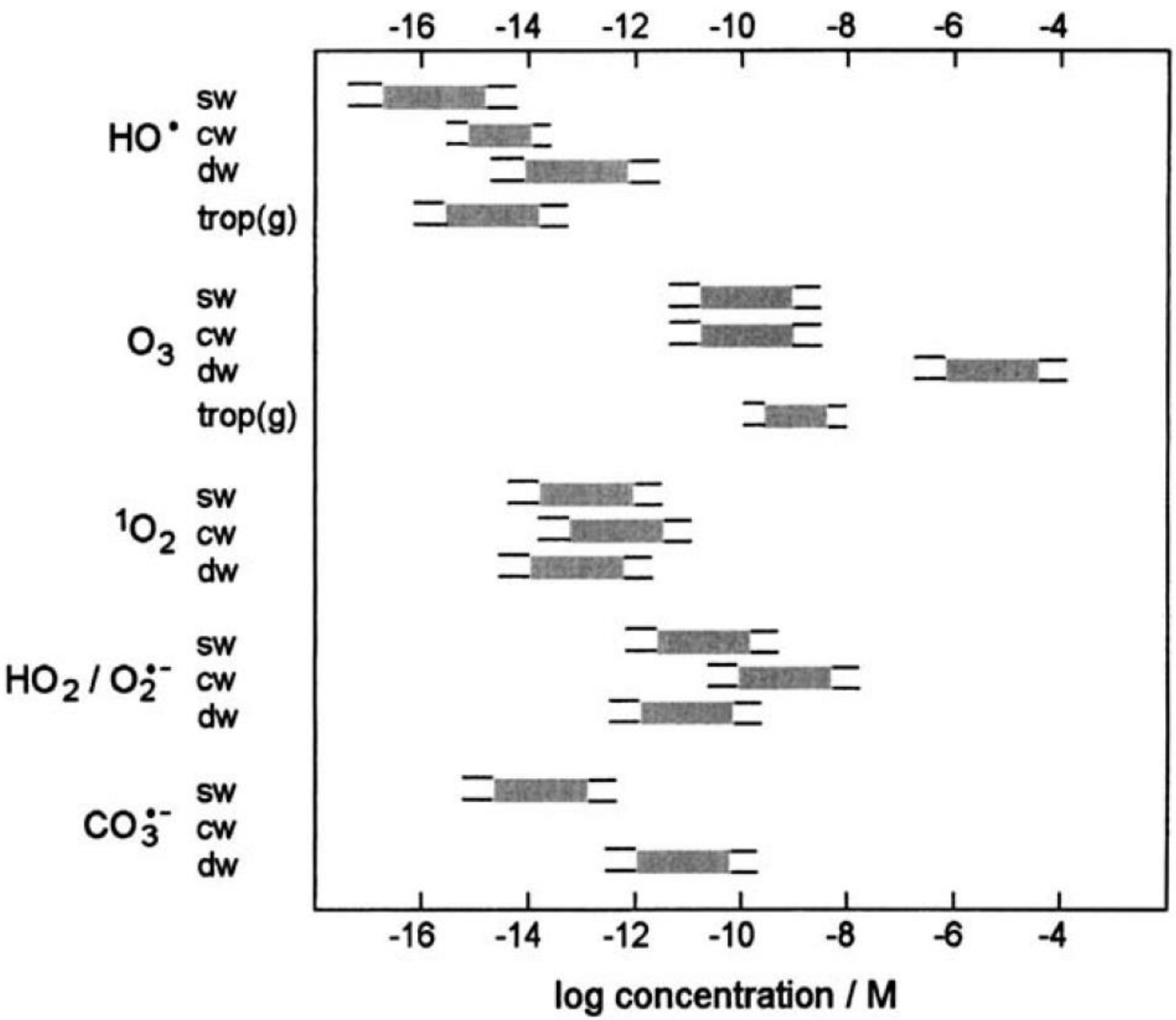


Figure 16.1 Ranges of steady-state concentrations of reactive oxygen species in sunlit surface waters (sw), sunlit cloud waters (cw), drinking-water treatment (dw), and the troposphere (trop(g)). Data from Sulzberger et al. (1997) and Atkinson et al. (1999).

16.2 Indirect Photolysis in Surface Waters

1. Overview

$$A + h\nu \rightarrow \text{Oxidants}$$

A: Light-absorbing species

e.g., NOM, NO_3^-, NO_2^-, Fe(III), H_2O_2, O_3 …

√ NOM

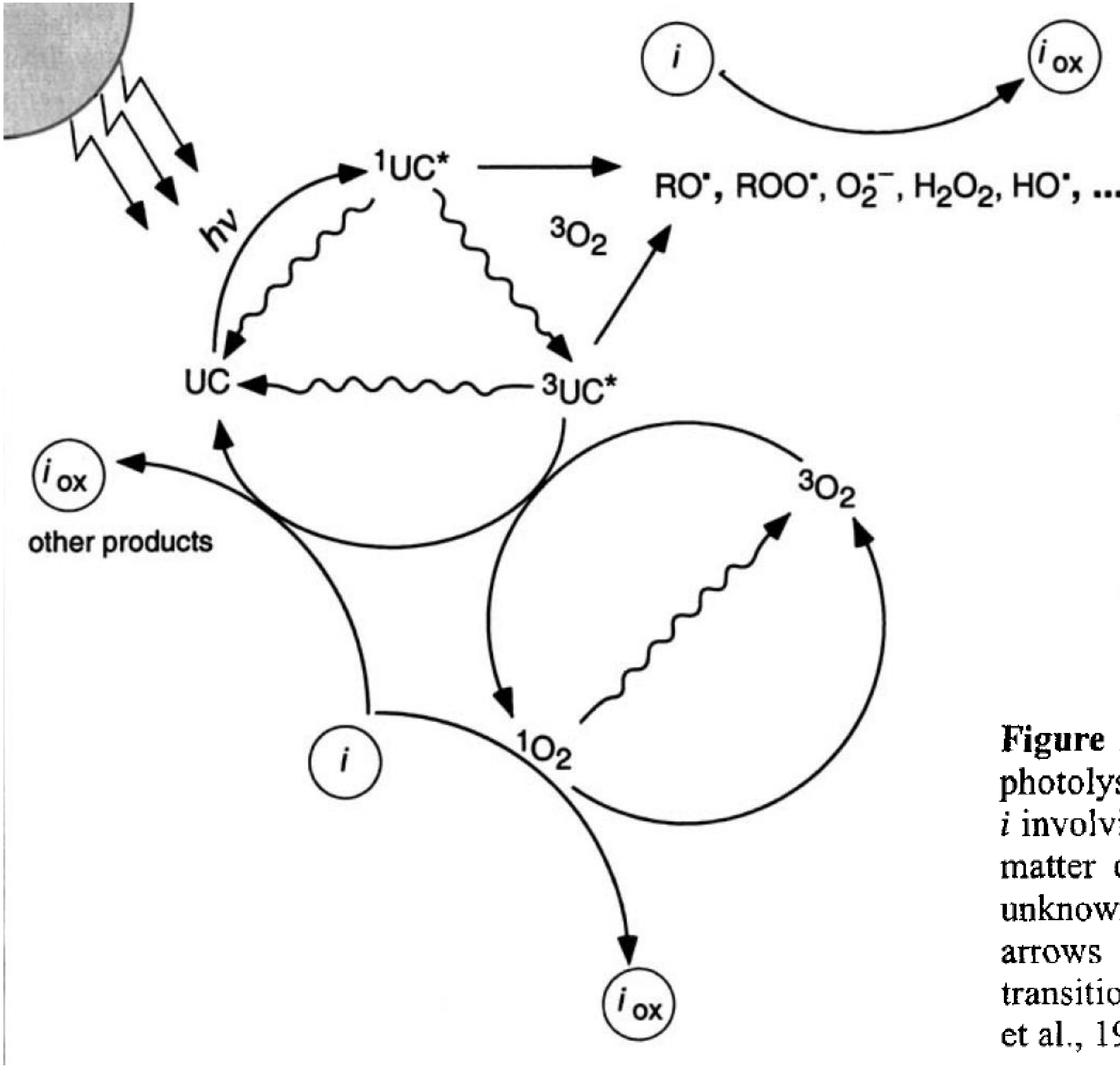


Figure 16.2 Pathways for indirect photolysis of an organic compound *i* involving excited natural organic matter constituents. UC refers to unknown chromophores. Wavy arrows symbolize radiationless transition (adapted from Zafiriou et al., 1984).

√ Nitrate, Nitrite

- Primary photochemical reaction

$$NO_3^- \xrightarrow{h\upsilon} NO_3^{-*} \longrightarrow NO_2 + O^{\bullet -} \xrightarrow{H_2O} HO^{\bullet} + OH^-$$

$$NO_2^- \xrightarrow{h\upsilon} NO_2^{-*} \longrightarrow NO + O^{\bullet -} \xrightarrow{H_2O} HO^{\bullet} + OH^-$$

- Secondary reactions (radical conversion)

$$HO^{\bullet} + HCO_3^- / CO_3^{2-} \rightarrow CO_3^{\bullet -} + H_2O / OH^-$$

$$HO^{\bullet} + Br^- \rightarrow Br^{\bullet} + OH^-$$

√ Fe(III)

- Ligand-to-Metal Charge Transfer (LMCT)
- Fe(III)-hydroxo complexes

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + \bullet OH + H^+$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + \bullet OH$$

$$Fe_2(OH)_2^{4+} + h\nu \rightarrow Fe(III) + Fe^{2+} + \bullet OH$$

- Other ferric complexes

$$Fe^{3+}(X) + h\nu \rightarrow Fe^{2+} + X\bullet$$

Ex) $Fe(SO_4)^+ + h\nu \rightarrow Fe^{2+} + SO_4^{-}\bullet$

$Fe(Cl)^{2+} + h\nu \rightarrow Fe^{2+} + Cl\bullet$

$Fe(Ox)_3^{3-} + h\nu \rightarrow Fe^{2+} + 2C_2O_4^{2-} + C_2O_4^{-}\bullet$

√ H_2O_2

$$H_2O_2 + hv \rightarrow 2{}^\bullet OH$$

Primary quantum yield: 0.5

$$H_2O_2 + hv \leftrightarrow [HO^\bullet + {}^\bullet OH] \rightarrow 2{}^\bullet OH$$

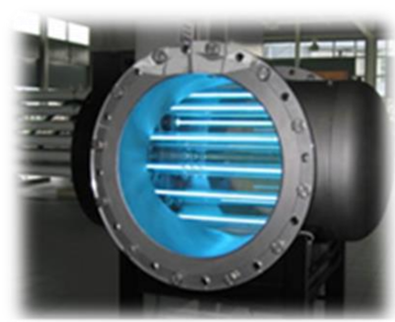
Solvent cage

Secondary reactions: $${}^\bullet OH + H_2O_2 \rightarrow HO_2\bullet + H_2O$$

$$2HO_2\bullet \rightarrow H_2O_2 + O_2$$

$$2\bullet OH \rightarrow H_2O_2$$

*UV/H_2O_2 process
for drinking water treatment



2. Kinetics

√ Photochemical degradation of pollutants by indirect photolysis in natural water

$$A + h\nu \rightarrow \text{Oxidant (Ox)}$$

$$\text{Oxidant (Ox)} + \text{Compound (C)} \xrightarrow{k_1} \text{Product}_1$$

$$\text{Oxidant (Ox)} + \text{Scavenger (S)} \xrightarrow{k_2} \text{Product}_2$$

d[A]/dt = ???

3. Reactions with •OH

√ Reactivity of •OH

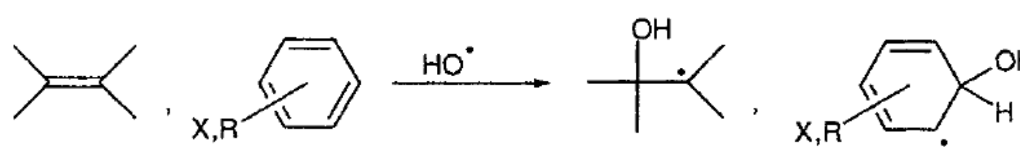
- Very reactive oxidant, $E^{o}(\bullet OH/H_2O) = 2.8\ V_{NHE}$
- Very fast reactions with almost all of organic compounds
  $k = 10^{8} \sim 10^{10}\ M^{-1}\ s^{-1}$
- Very low steady-state concentration in natural water
  $[\bullet OH]_{ss} = 10^{-16} \sim 10^{-12}\ M$

√ Reaction mechanism of •OH

- H-Abstraction

$$R-H \xrightarrow{HO^{\bullet}} R^{\bullet} + H_2O$$

- e^{-}-Abstraction
- Addition



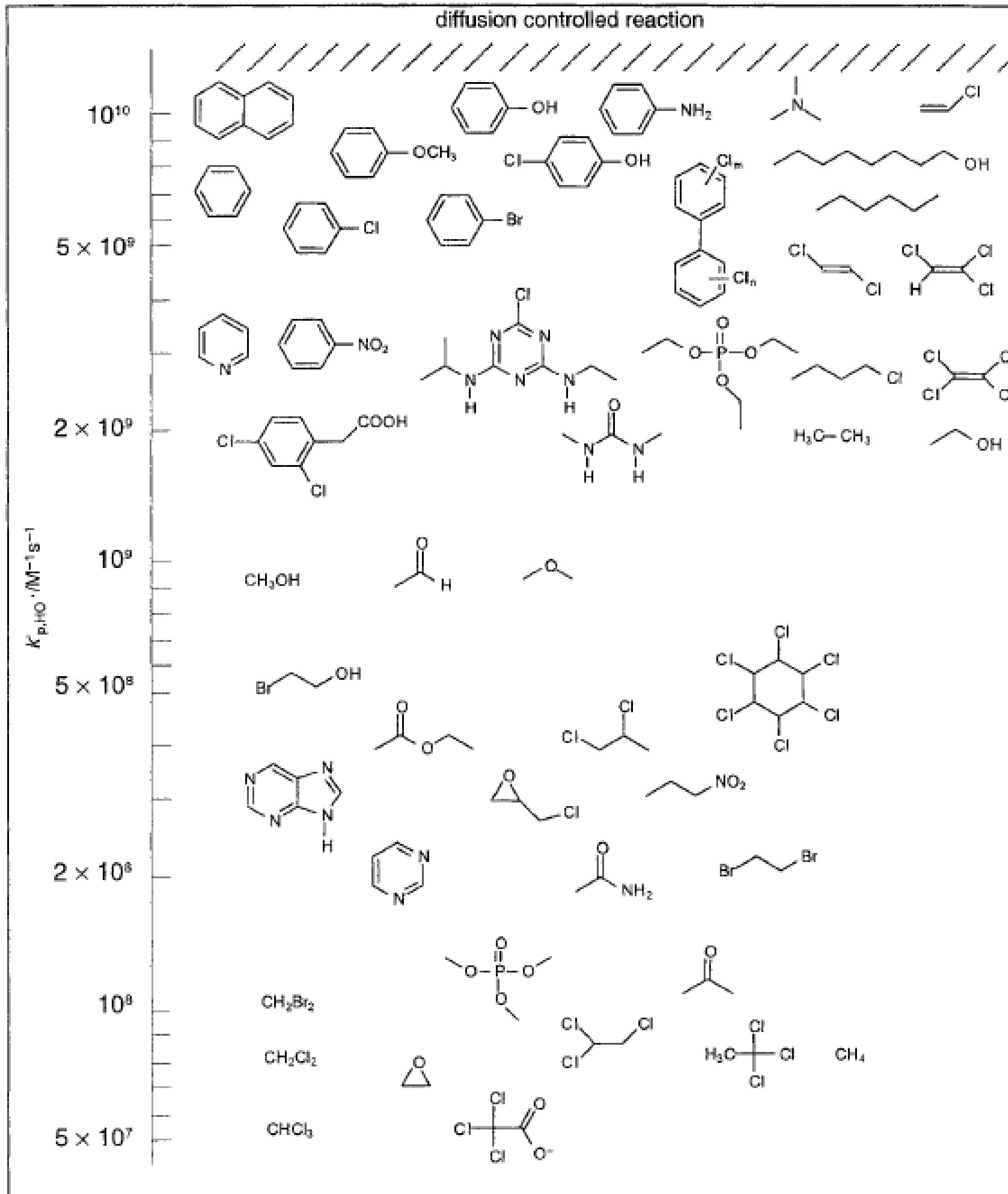


Figure 16.3 Second-order rate constants for reaction with $HO^\bullet$ in aqueous solution ($k'_{p,HO^\bullet}$; Eq. 16-7) for a series of organic compounds. Data from http://allen.rad.nd.edu, and Haag and Yao (1992).

4. Reactions with $^1O_2$

√ Reactivity of $^1O_2$

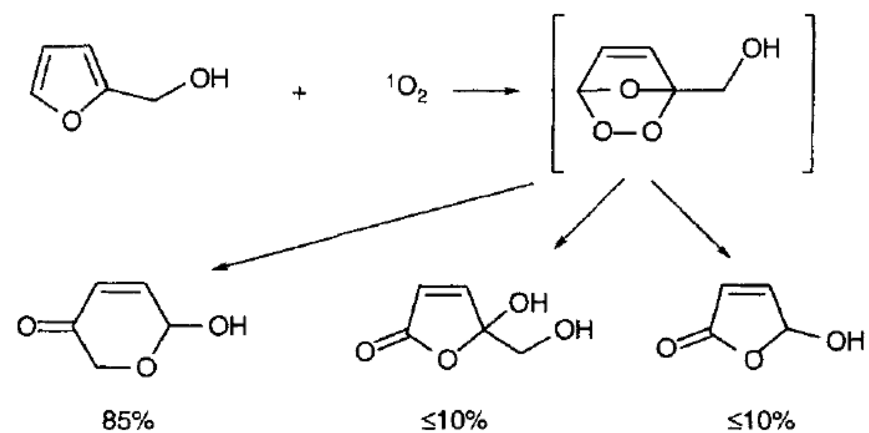
- Still strong, but relatively weaker oxidant compared to $^{\bullet}OH$
- Relatively slower reactions compared to $^{\bullet}OH$

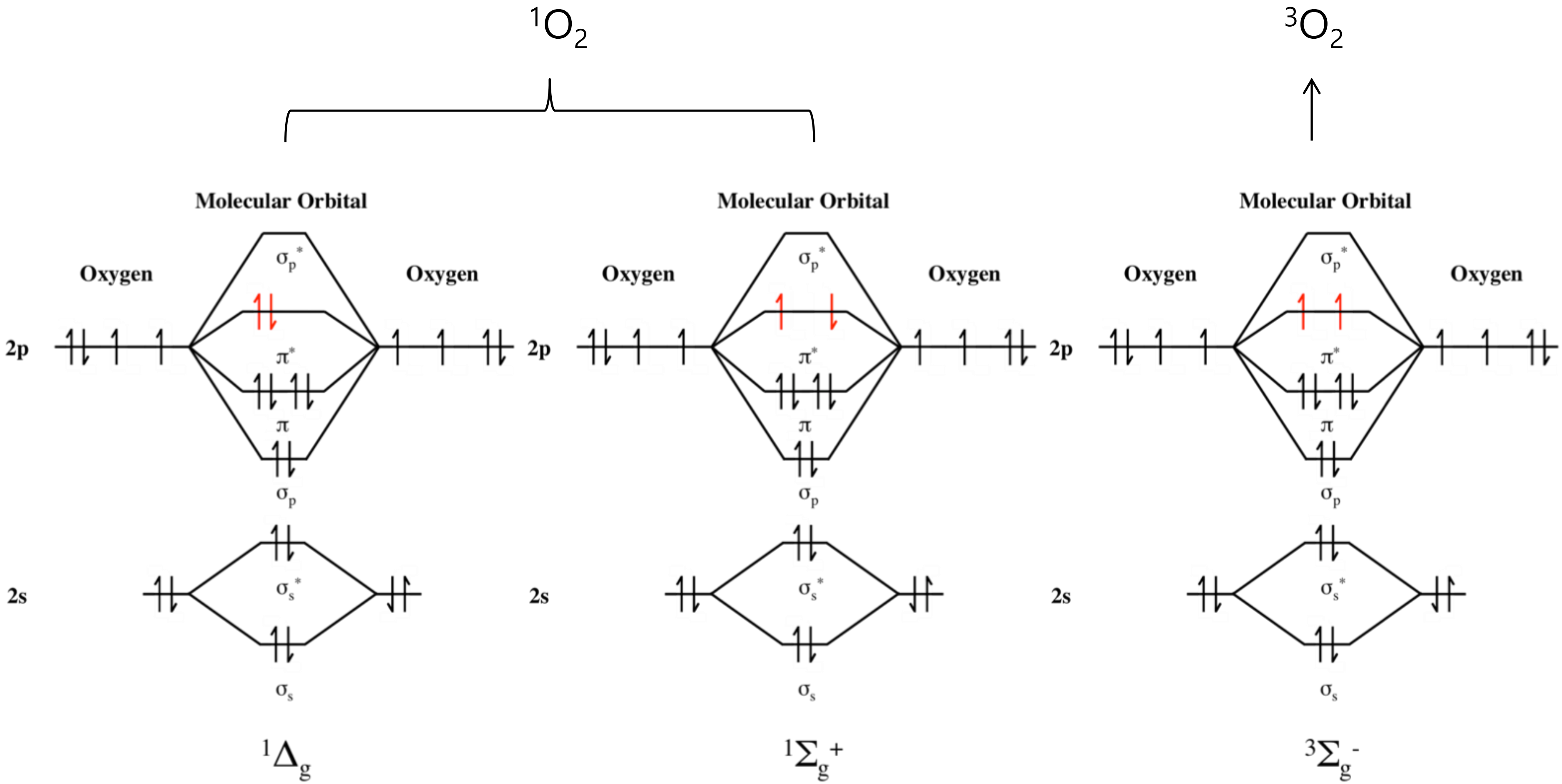
  k = 1~10^8 M^{-1} s^{-1}
- Slightly higher steady-state concentration in natural water

  $[^1O_2]_{ss}$ = 10^{-14} ~ 10^{-12} M

√ Reaction mechanism of $^1O_2$

- Addition





1O2
3O2
Molecular Orbital
Oxygen
Oxygen
2p
2s
σp*
π*
π
σp
σs*
σs
1Δg
Molecular Orbital
Oxygen
Oxygen
2p
2s
σp*
π*
π
σp
σs*
σs
1Σg+
Molecular Orbital
Oxygen
Oxygen
2p
2s
σp*
π*
π
σp
σs*
σs
3Σg-

5. Reactions with $^3DOM^*$, $R^\bullet$, $RO^\bullet$, $ROO^\bullet$

√ NOM

$$DOM + h\nu \rightarrow {}^3DOM^*$$

$$^3DOM^* + \text{Compound} \rightarrow \text{Products}$$

- H-Abstraction } oxidation
- e^--Abstraction } oxidation
- Energy transfer (e.g., isomerization)

√ $R^\bullet$, $RO^\bullet$, $ROO^\bullet$

$$RH + {}^\bullet OH \rightarrow R^\bullet$$

$$R^\bullet + O_2 \rightarrow ROO^\bullet$$

$$2ROO^\bullet \rightarrow 2RO^\bullet + O_2$$

$$ROO^\bullet \text{ or } RO^\bullet + \text{Compound} \rightarrow \text{Products}$$