Biological Transformation Reactions

Biodegradation:

1. Primary biodegradation;
2. Ultimate biodegradation; and
3. Acceptable biodegradation.

Xenobiotic organic compounds

Enzyme

Michaelis-Menten kinetics

Microbial population

Monod kinetics

Biological transformation agents for the Xenobiotic organic compounds

1. Plants;
2. Animals; and
3. Microorganisms.

The types of microorganisms are environmental condition dependent. However, many microorganisms exhibit similar biochemical pathways and capabilities. The ultimate degradation of an organic compound may not be performed by a single microorganism.

Important environmental factors for the types of microorganisms present are temperature, pH, strength, oxygen concentration, etc. (e.g., Fig. 14.3)

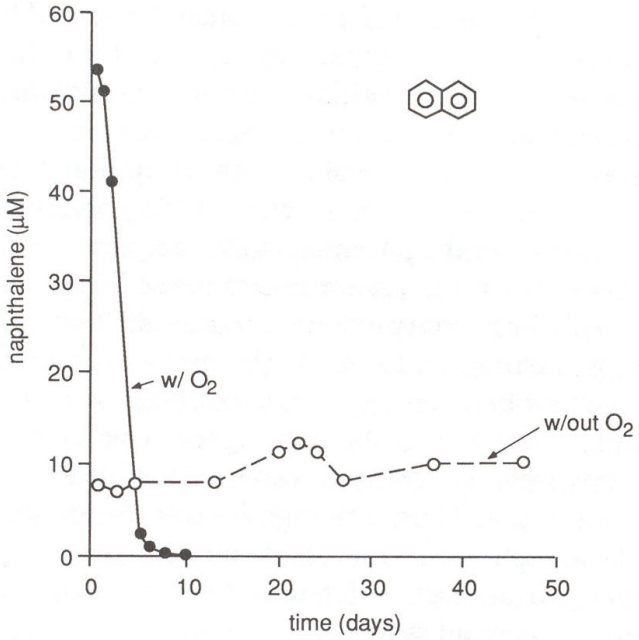

Figure 14.3 Variation in timecourses of naphthalene degradation by microorganisms in laboratory soil–water incubations with molecular oxygen present (●) or no molecular oxygen present (○) (data from Mihelcic and Luthy, 1988).

from Schwarzenbach, R. P., Gschwend, P. M., and Imboden, D. M. (1993) Environmental Organic Chemistry, John Wiley & Sons

Enzyme

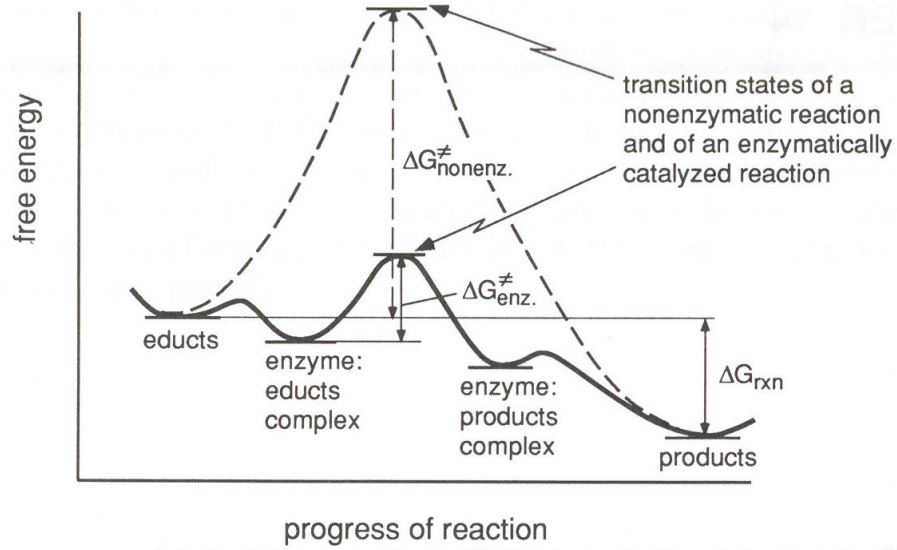

Figure 14.1 Schematic representation of the change in activation energy barriers for an enzymatically mediated reaction as compared to the analogous noncatalyzed chemical reaction.

from Schwarzenbach, R. P., Gschwend, P. M., and Imboden, D. M. (1993) Environmental Organic Chemistry, John Wiley & Sons

Enzyme inhibitions

When E = enzyme; S = substrate; I = inhibitor; and
ES = enzyme-substrate complex;

<u>Competitive inhibition;</u>

$E + S \leftrightarrow ES \rightarrow E + P$

$E + I \leftrightarrow EI$

<u>Uncompetitive inhibition;</u>

$E + S \leftrightarrow ES \rightarrow E + P$

$ES + I \leftrightarrow ESI$

Noncompetitive inhibition;

$E + S \leftrightarrow ES \rightarrow E + P$

$E + I \leftrightarrow EI$

$ES + I \leftrightarrow ESI$

Substrate inhibition;

$E + S \leftrightarrow ES \rightarrow E + P$

$ES + S \leftrightarrow SES$

Product inhibition;

$E + S \leftrightarrow ES \rightarrow E + P$

$ES + P \leftrightarrow ESP$

Michaelis-Menten Kinetics

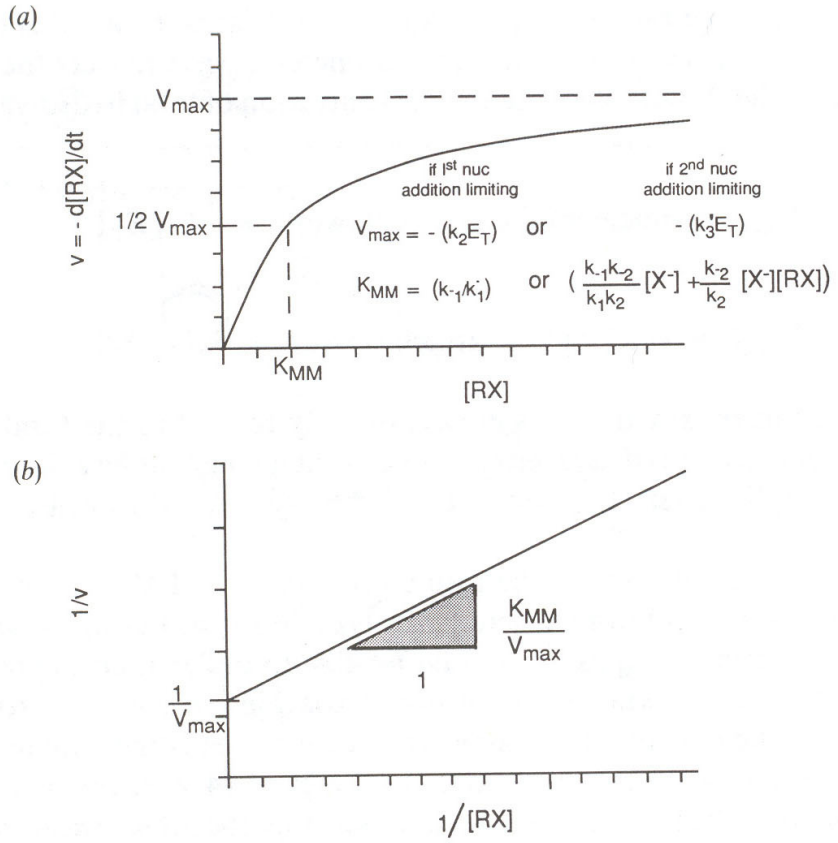

Figure 14.13 Relationships of biodegradation rate, $v = -[R-X]/dt$, to substrate concentration $[R-X]$ when Michaelis–Menton type enzyme kinetics is appropriate: (*a*) when plotted as hyperbolic relationship (Eq. 14-91 in text), or (*b*) when plotted as inverse equation, $1/v = (K_{MM}/V_{max})/[R-X] + (1/V_{max})$. Factors governing V_{max} and K_{MM} differ depending on rate-limiting step in the enzymatic sequence.

from Schwarzenbach, R. P., Gschwend, P. M., and Imboden, D. M. (1993) Environmental Organic Chemistry, John Wiley & Sons

where v = rate of substrate removal (= - dS/dt);

V_{max} = fastest possible substrate removal rate; and

K_{MM} = concentration of substrate at $v = V_{max}/2$.

TABLE 14.9 Apparent Michaelis Menten Parameters Reported for Microbial Degradation of Various Substrates[a]

Substrate	K_{MM}	V_{max} (mol·kg^{-1}protein·s^{-1})	Reference
		A. Natural populations	
Toluene in seawater	18 nM	6×10^{-10} $\left(1.5 \frac{\text{pmol}}{\text{L·h}}\right)$	Reichardt et al., 1981
Biphenyl in seawater	1.5 nM	4×10^{-8} $\left(100 \frac{\text{pmol}}{\text{L·h}}\right)$	
m-Cresol in estuarine seawater	6–17 nM	$5–4000 \times 10^{-9}$ $\left(4–1300 \frac{\text{pmol}}{\text{L·h}}\right)$	Bartholomew and Pfaender, 1983
Chlorobenzene in estuarine seawater	9–46 nM	$2–4 \times 10^{-8}$ $\left(15–130 \frac{\text{pmol}}{\text{L·h}}\right)$	
Trichlorobenzene in estuarine seawater	25–38 nM	$1–2 \times 10^{-8}$ $\left(13–43 \frac{\text{pmol}}{\text{L·h}}\right)$	
Nitrilotriacetic acid in estuarine seawater	290–580 nM	$4–400 \times 10^{-7}$ $\left(300–2600 \frac{\text{pmol}}{\text{L·h}}\right)$	

from Schwarzenbach, R. P., Gschwend, P. M., and Imboden, D. M. (1993) Environmental Organic Chemistry, John Wiley & Sons

Monod Kinetics

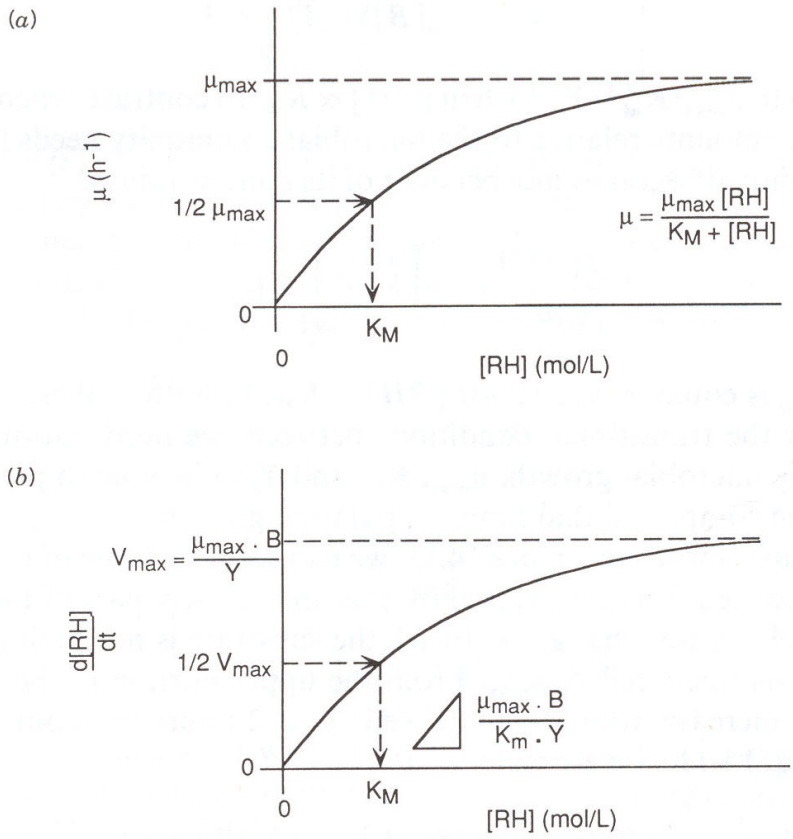

Figure 14.16 Schematic relationships of: (*a*) microbial population specific growth rate μ versus substrate concentration after Monod (1949), and (*b*) consequent substrate disappearance rate, $d[RH]/dt$, versus substrate concentration.

from Schwarzenbach, R. P., Gschwend, P. M., and Imboden, D. M. (1993) Environmental Organic Chemistry, John Wiley & Sons

To quantify the microbial population dynamics in the system.

where X = cell concentration (or cell abundance); and

μ = specific growth rate [T^{-1}];

where μ_{max} = maximum growth rate [T^{-1}]; and

K_M = Monod constant.

(concentration of substrate at $\mu = \mu_{max}/2$)

where Y = yield of the biological process.

New cell production rate,

and

$$\frac{dS}{dt} = -\frac{\mu_{max} \cdot X \cdot Y^{-1} \cdot S}{K_M + S}$$

If $S << K_M$,

$$\frac{dS}{dt} = -\frac{\mu_{max} \cdot X \cdot Y^{-1} \cdot S}{K_M} = -\frac{\mu_{max}}{K_M \cdot Y} \cdot X \cdot S = k_{bio} \cdot X \cdot S$$

If $S >> K_M$,

$$\frac{dS}{dt} = -\frac{\mu_{max} \cdot X \cdot Y^{-1} \cdot S}{S} = -\frac{\mu_{max}}{Y} \cdot X$$

TABLE 14.10 Some Monod Biodegradation Parameters Obtained from Enrichment Cultures Grown on the Substrate Indicated

Substrate	Source of Microorganisms	μ_{max} (h^{-1})	K_M (μM)	Y (cells/mol)	Reference
Malathion	Bacterial enrichments from river water	0.37	2.2	4×10^{10}	Paris et al., 1975
p-Cresol	Bacterial enrichments from pond water	0.69	6.4	2×10^{14}	Smith et al., 1978
Quinoline	Enrichments from pond	0.74	1.2	2×10^{14}	Smith et al., 1978
Methyl parathion	Enrichments from creek	0.61	10	2×10^{14}	
Methylene chloride	Enrichments of *Pseudomonas sp.* mutants	0.11	—	$\approx \frac{10^{13}-10^{14}}{\text{mol}}$	Brunner et al., 1980
Glycerol	Pure cultures				
	Aerobacter	1.2	120		Jannasch, 1967
	Achromobacter	0.55	11		
Glucose	Pure cultures				
	Vibrio, Aerobacter, Achromobacter, Escherichia coli	0.40–0.65	17–46		Jannasch, 1968

from Schwarzenbach, R. P., Gschwend, P. M., and Imboden, D. M. (1993) Environmental Organic Chemistry, John Wiley & Sons

The time for biodegradation to remove a xenobiotic compound:

$$X_{crit} \cong S_o \cdot Y$$

$$t_{crit} \cong ln\left(\frac{X_{crit}}{X_o}\right) / \mu_{max}$$