Part 3. The Terrestrial Environment

Chapter 20. Organic Biocides

Chapter 20. Organic Biocides

20.0 Generals: example of biocides (xenobiotics)

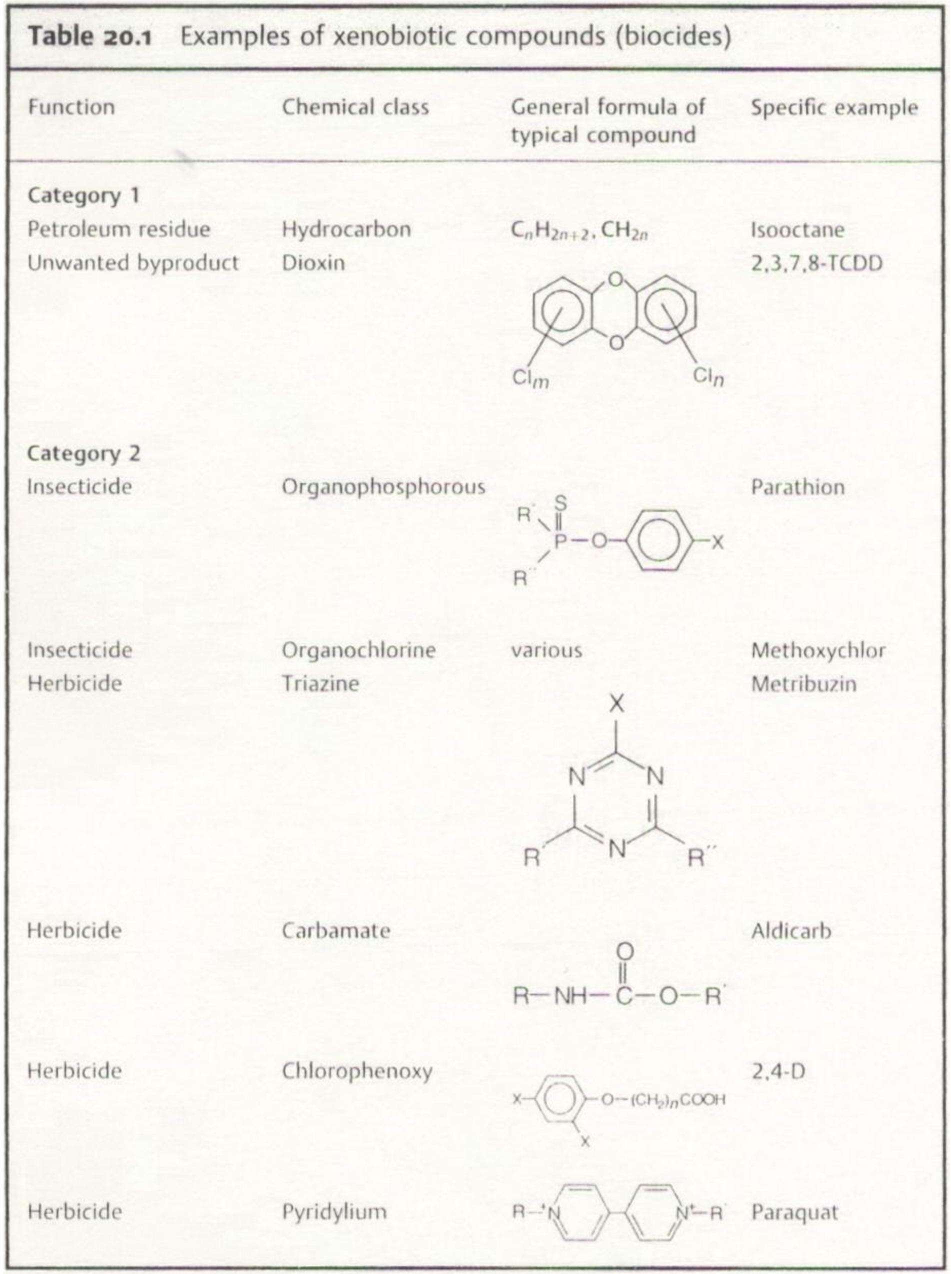

Table 20.1 Examples of xenobiotic compounds (biocides)

Function	Chemical class	General formula of typical compound	Specific example
Category 1			
Petroleum residue	Hydrocarbon	C_nH_{2n+2}, CH_{2n}	Isooctane
Unwanted byproduct	Dioxin		2,3,7,8-TCDD
Category 2			
Insecticide	Organophosphorous		Parathion
Insecticide	Organochlorine	various	Methoxychlor
Herbicide	Triazine		Metribuzin
Herbicide	Carbamate	$R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}O{-}R'$	Aldicarb
Herbicide	Chlorophenoxy		2,4-D
Herbicide	Pyridylium		Paraquat

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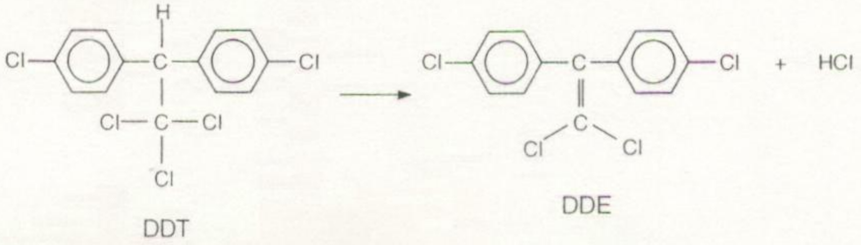
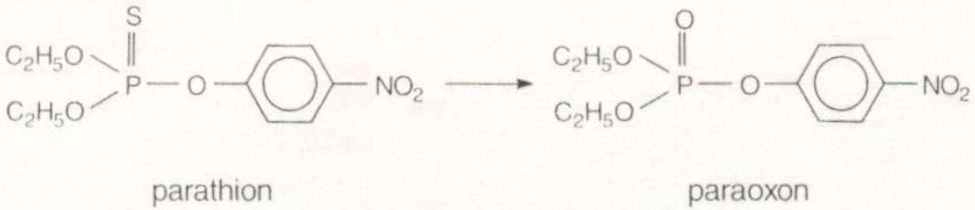
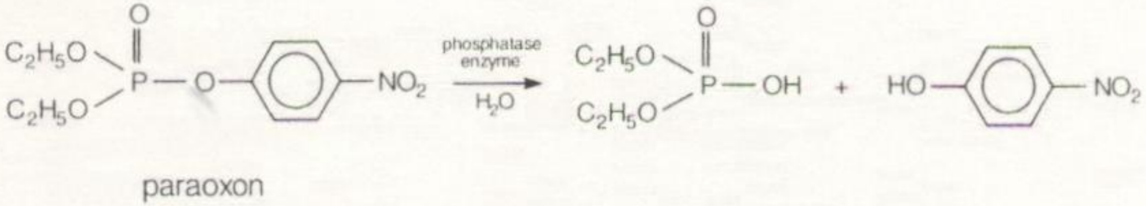
20.1 Chemical Stability: example of chemical degradations



(20.1)



(20.2)



(20.3)

Enzyme: acetylcholinesterase (AcE)

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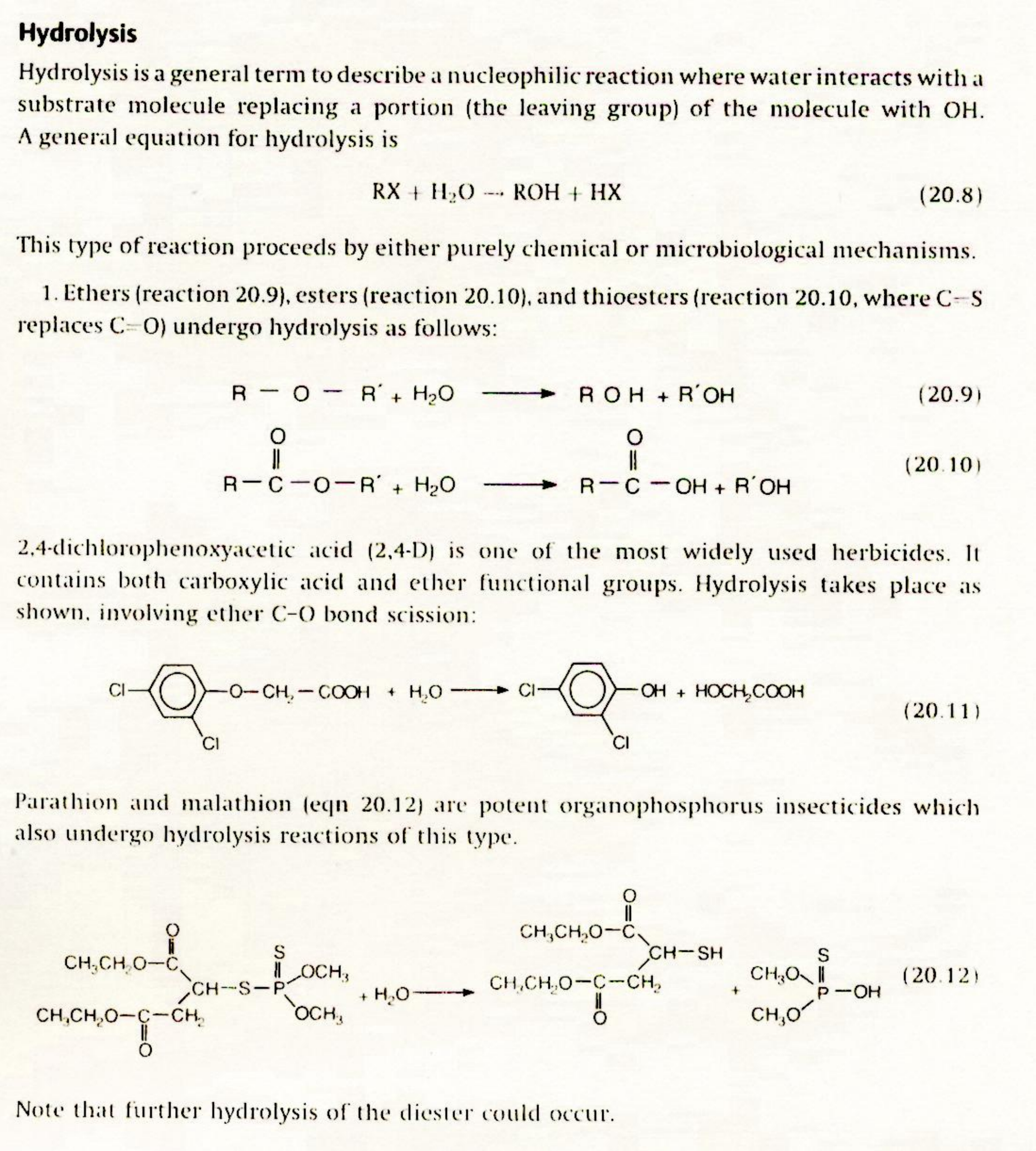
20.1 Chemical Stability: non-photolytic reaction



Hydrolysis

Hydrolysis is a general term to describe a nucleophilic reaction where water interacts with a substrate molecule replacing a portion (the leaving group) of the molecule with OH. A general equation for hydrolysis is

$$RX + H_2O \rightarrow ROH + HX \qquad (20.8)$$

This type of reaction proceeds by either purely chemical or microbiological mechanisms.

1. Ethers (reaction 20.9), esters (reaction 20.10), and thioesters (reaction 20.10, where C=S replaces C=O) undergo hydrolysis as follows:

$$R-O-R' + H_2O \longrightarrow ROH + R'OH \qquad (20.9)$$

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R' + H_2O \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + R'OH \qquad (20.10)$$

2,4-dichlorophenoxyacetic acid (2,4-D) is one of the most widely used herbicides. It contains both carboxylic acid and ether functional groups. Hydrolysis takes place as shown, involving ether C–O bond scission:

(20.11)

Parathion and malathion (eqn 20.12) are potent organophosphorus insecticides which also undergo hydrolysis reactions of this type.

(20.12)

Note that further hydrolysis of the diester could occur.

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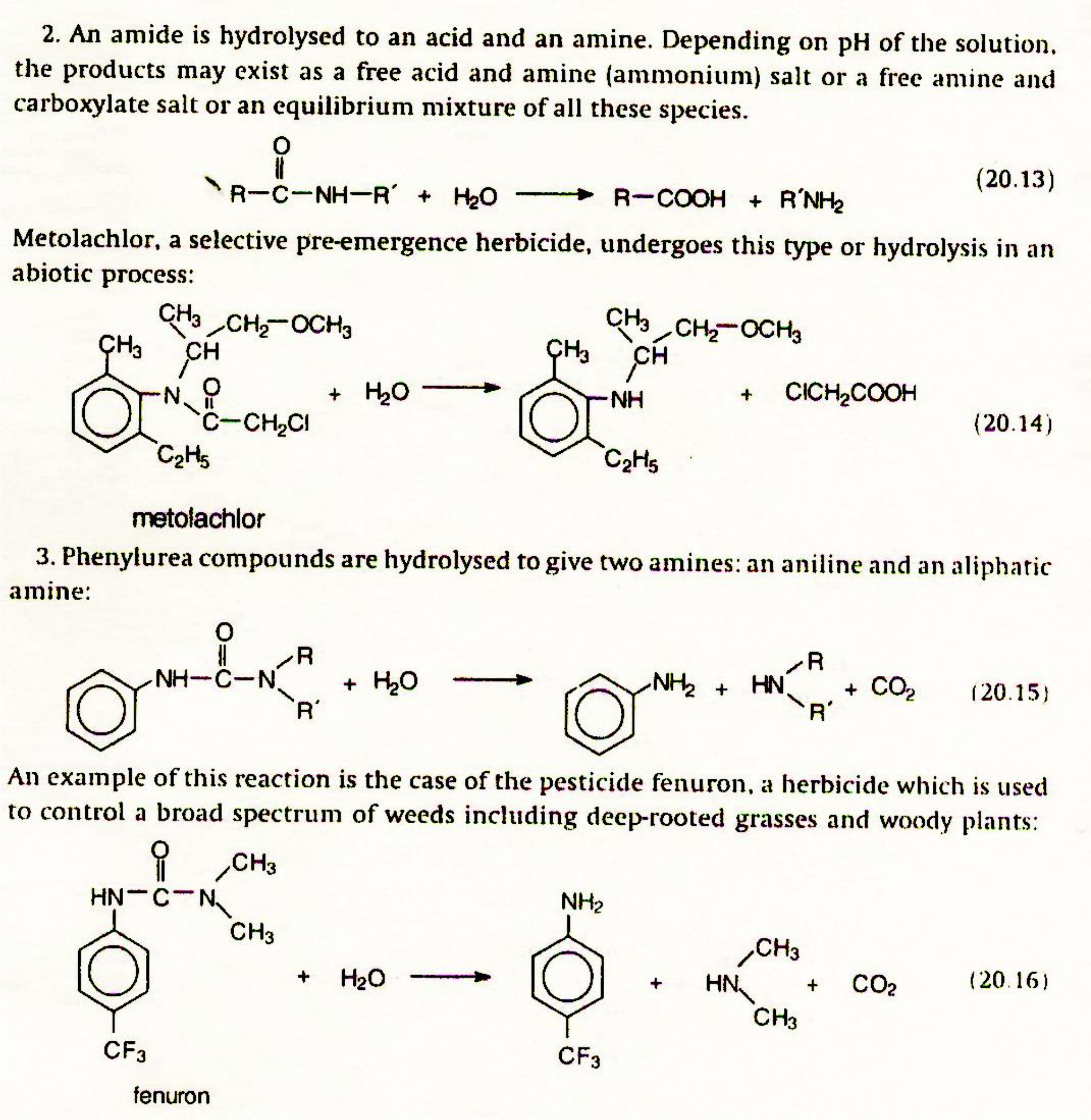
20.1 Chemical Stability: non-photolytic reaction



2. An amide is hydrolysed to an acid and an amine. Depending on pH of the solution, the products may exist as a free acid and amine (ammonium) salt or a free amine and carboxylate salt or an equilibrium mixture of all these species.

$$R{-}\overset{O}{\overset{\|}{C}}{-}NH{-}R' + H_2O \longrightarrow R{-}COOH + R'NH_2 \qquad (20.13)$$

Metolachlor, a selective pre-emergence herbicide, undergoes this type or hydrolysis in an abiotic process:

(20.14)

metolachlor

3. Phenylurea compounds are hydrolysed to give two amines: an aniline and an aliphatic amine:

(20.15)

An example of this reaction is the case of the pesticide fenuron, a herbicide which is used to control a broad spectrum of weeds including deep-rooted grasses and woody plants:

(20.16)

fenuron

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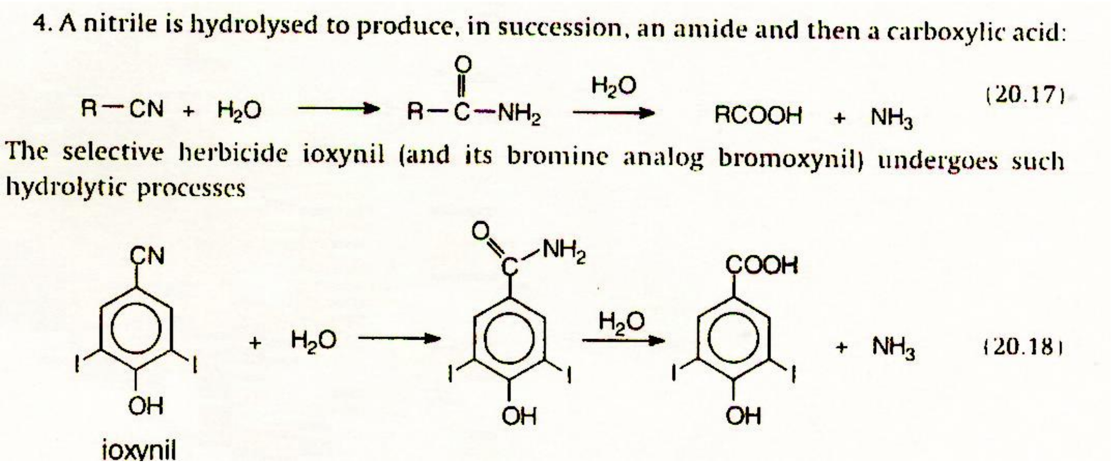
20.1 Chemical Stability: non-photolytic reaction

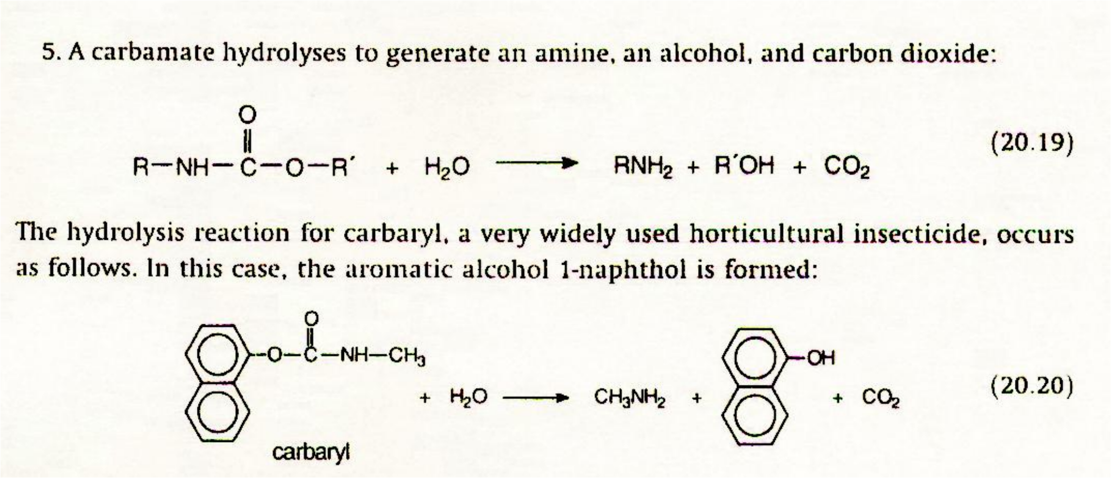


4. A nitrile is hydrolysed to produce, in succession, an amide and then a carboxylic acid:

$$R-CN + H_2O \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow{H_2O} RCOOH + NH_3 \qquad (20.17)$$

The selective herbicide ioxynil (and its bromine analog bromoxynil) undergoes such hydrolytic processes

(20.18)



5. A carbamate hydrolyses to generate an amine, an alcohol, and carbon dioxide:

$$R-NH-\overset{\overset{\displaystyle O}{\|}}{C}-O-R' + H_2O \longrightarrow RNH_2 + R'OH + CO_2 \qquad (20.19)$$

The hydrolysis reaction for carbaryl, a very widely used horticultural insecticide, occurs as follows. In this case, the aromatic alcohol 1-naphthol is formed:

(20.20)

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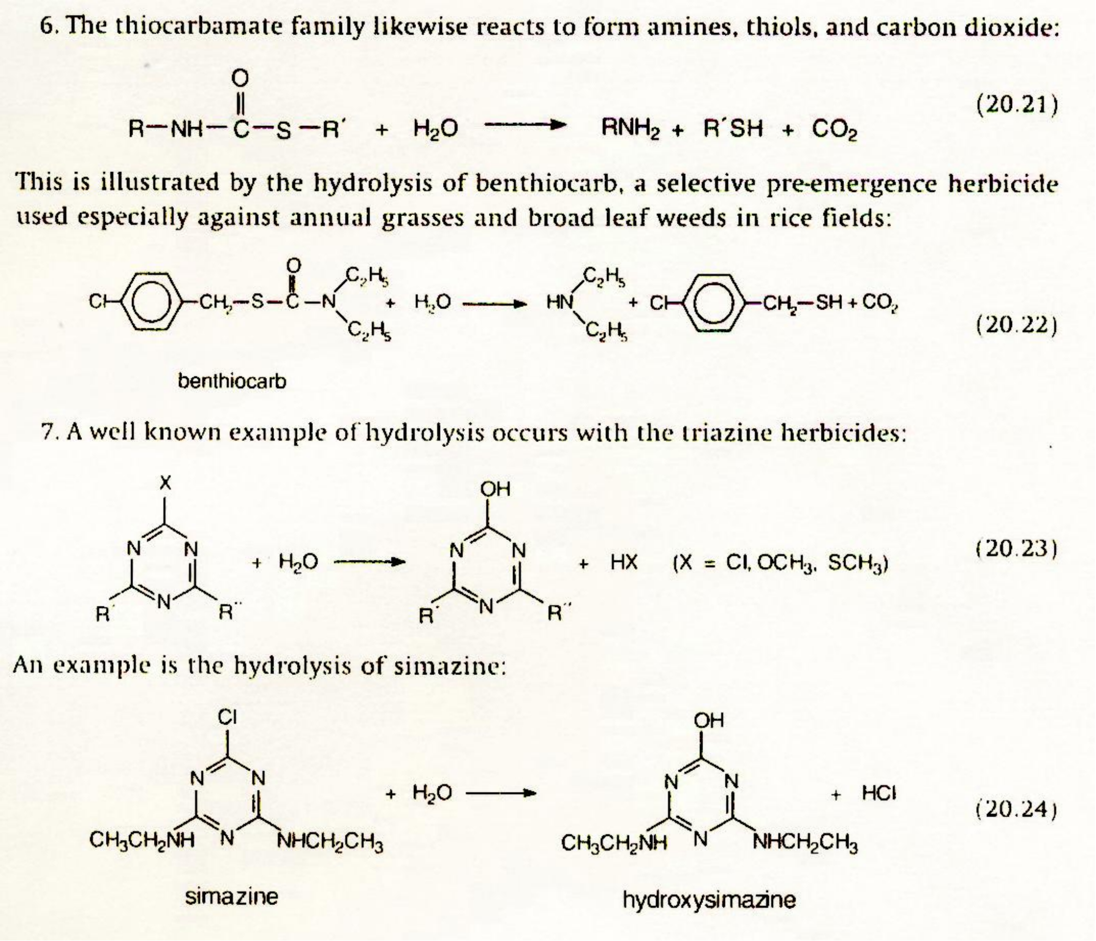
20.1 Chemical Stability: non-photolytic reaction



6. The thiocarbamate family likewise reacts to form amines, thiols, and carbon dioxide:

$$R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}S{-}R' + H_2O \longrightarrow RNH_2 + R'SH + CO_2 \qquad (20.21)$$

This is illustrated by the hydrolysis of benthiocarb, a selective pre-emergence herbicide used especially against annual grasses and broad leaf weeds in rice fields:

(20.22)

benthiocarb

7. A well known example of hydrolysis occurs with the triazine herbicides:

(20.23)

An example is the hydrolysis of simazine:

(20.24)

simazine

hydroxysimazine

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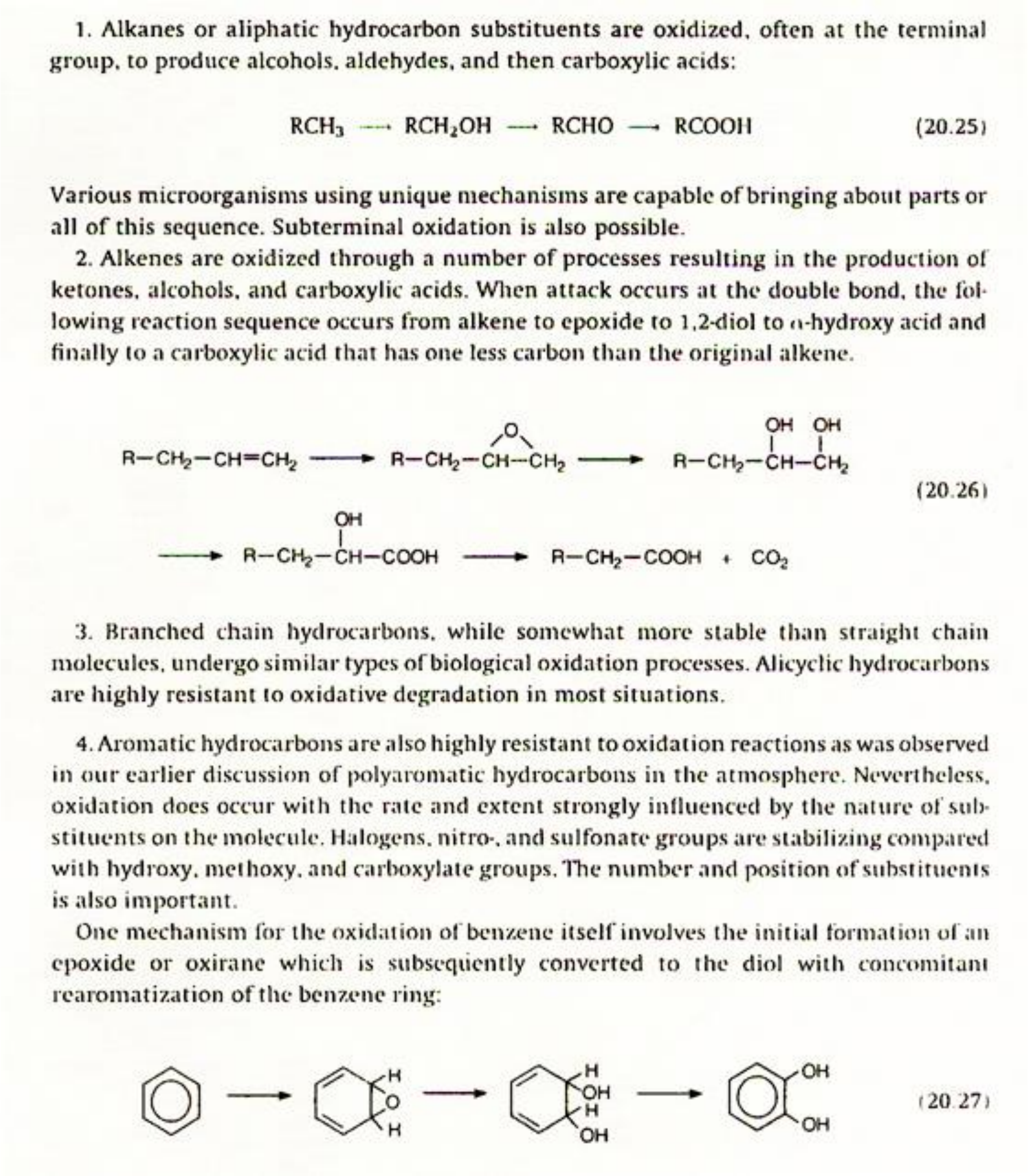
20.1 Chemical Stability: non-photolytic reaction

Oxidation



1. Alkanes or aliphatic hydrocarbon substituents are oxidized, often at the terminal group, to produce alcohols, aldehydes, and then carboxylic acids:

$$RCH_3 \longrightarrow RCH_2OH \longrightarrow RCHO \longrightarrow RCOOH \qquad (20.25)$$

Various microorganisms using unique mechanisms are capable of bringing about parts or all of this sequence. Subterminal oxidation is also possible.

2. Alkenes are oxidized through a number of processes resulting in the production of ketones, alcohols, and carboxylic acids. When attack occurs at the double bond, the following reaction sequence occurs from alkene to epoxide to 1,2-diol to α-hydroxy acid and finally to a carboxylic acid that has one less carbon than the original alkene.

$$R{-}CH_2{-}CH{=}CH_2 \longrightarrow R{-}CH_2{-}\overbrace{CH{-}CH_2}^{O} \longrightarrow R{-}CH_2{-}\overset{OH}{\overset{|}{C}H}{-}\overset{OH}{\overset{|}{C}H_2} \qquad (20.26)$$

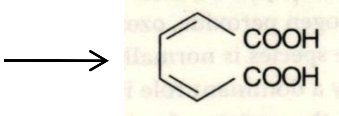
$$\longrightarrow R{-}CH_2{-}\overset{OH}{\overset{|}{C}H}{-}COOH \longrightarrow R{-}CH_2{-}COOH + CO_2$$

3. Branched chain hydrocarbons, while somewhat more stable than straight chain molecules, undergo similar types of biological oxidation processes. Alicyclic hydrocarbons are highly resistant to oxidative degradation in most situations.

4. Aromatic hydrocarbons are also highly resistant to oxidation reactions as was observed in our earlier discussion of polyaromatic hydrocarbons in the atmosphere. Nevertheless, oxidation does occur with the rate and extent strongly influenced by the nature of substituents on the molecule. Halogens, nitro-, and sulfonate groups are stabilizing compared with hydroxy, methoxy, and carboxylate groups. The number and position of substituents is also important.

One mechanism for the oxidation of benzene itself involves the initial formation of an epoxide or oxirane which is subsequently converted to the diol with concomitant rearomatization of the benzene ring:

(20.27)



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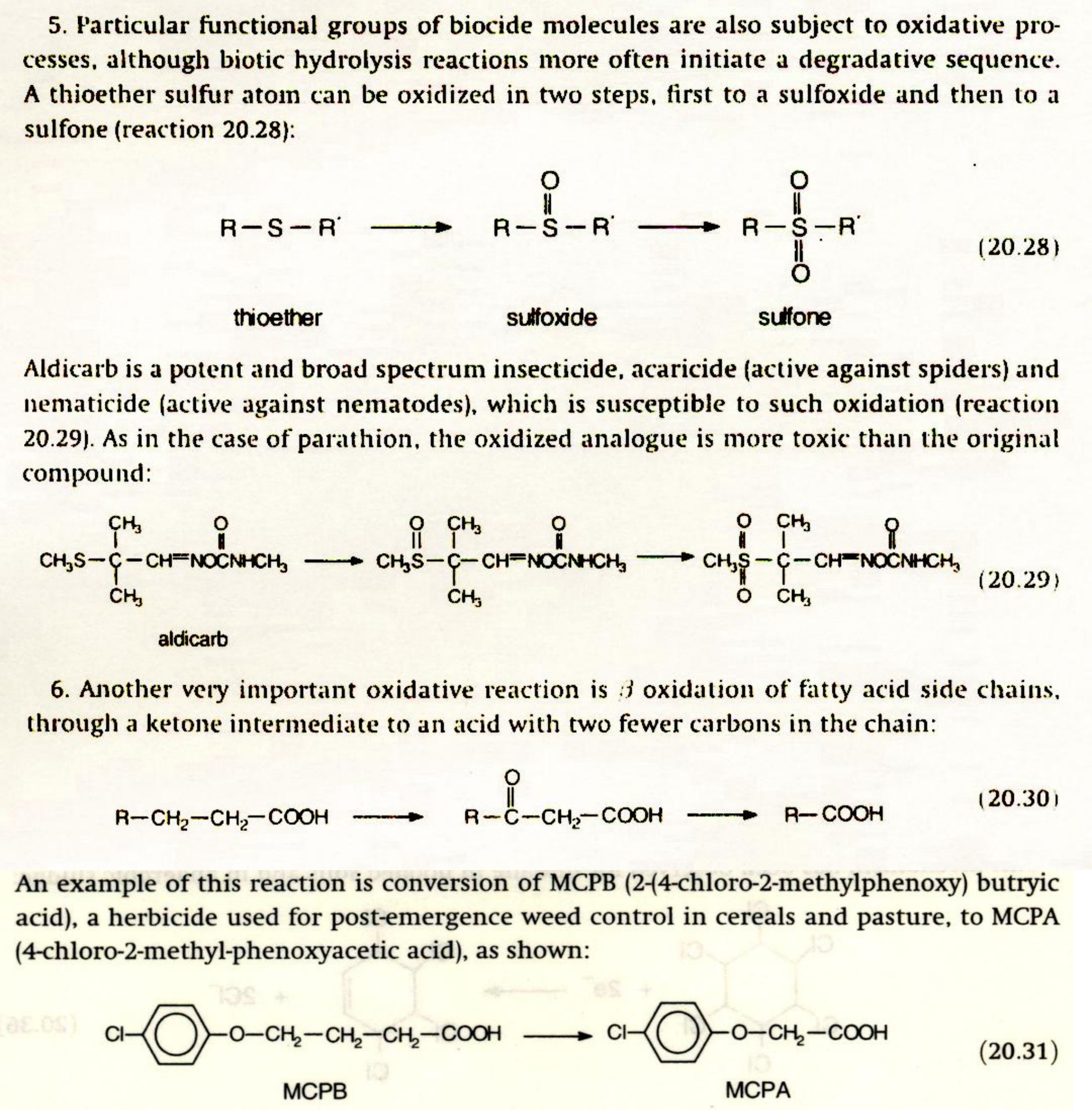
20.1 Chemical Stability: non-photolytic reaction

Oxidation



5. Particular functional groups of biocide molecules are also subject to oxidative processes, although biotic hydrolysis reactions more often initiate a degradative sequence. A thioether sulfur atom can be oxidized in two steps, first to a sulfoxide and then to a sulfone (reaction 20.28):

$$R{-}S{-}R' \longrightarrow R{-}\overset{O}{\overset{\|}{S}}{-}R' \longrightarrow R{-}\underset{\underset{O}{\|}}{\overset{O}{\overset{\|}{S}}}{-}R' \qquad (20.28)$$

thioether sulfoxide sulfone

Aldicarb is a potent and broad spectrum insecticide, acaricide (active against spiders) and nematicide (active against nematodes), which is susceptible to such oxidation (reaction 20.29). As in the case of parathion, the oxidized analogue is more toxic than the original compound:

$$CH_3S{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH{=}NO\overset{O}{\overset{\|}{C}}NHCH_3 \longrightarrow CH_3\overset{O}{\overset{\|}{S}}{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH{=}NO\overset{O}{\overset{\|}{C}}NHCH_3 \longrightarrow CH_3\underset{\underset{O}{\|}}{\overset{O}{\overset{\|}{S}}}{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH{=}NO\overset{O}{\overset{\|}{C}}NHCH_3 \qquad (20.29)$$

aldicarb

6. Another very important oxidative reaction is β oxidation of fatty acid side chains, through a ketone intermediate to an acid with two fewer carbons in the chain:

$$R{-}CH_2{-}CH_2{-}COOH \longrightarrow R{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}COOH \longrightarrow R{-}COOH \qquad (20.30)$$

An example of this reaction is conversion of MCPB (2-(4-chloro-2-methylphenoxy) butryic acid), a herbicide used for post-emergence weed control in cereals and pasture, to MCPA (4-chloro-2-methyl-phenoxyacetic acid), as shown:

(20.31)

MCPB MCPA

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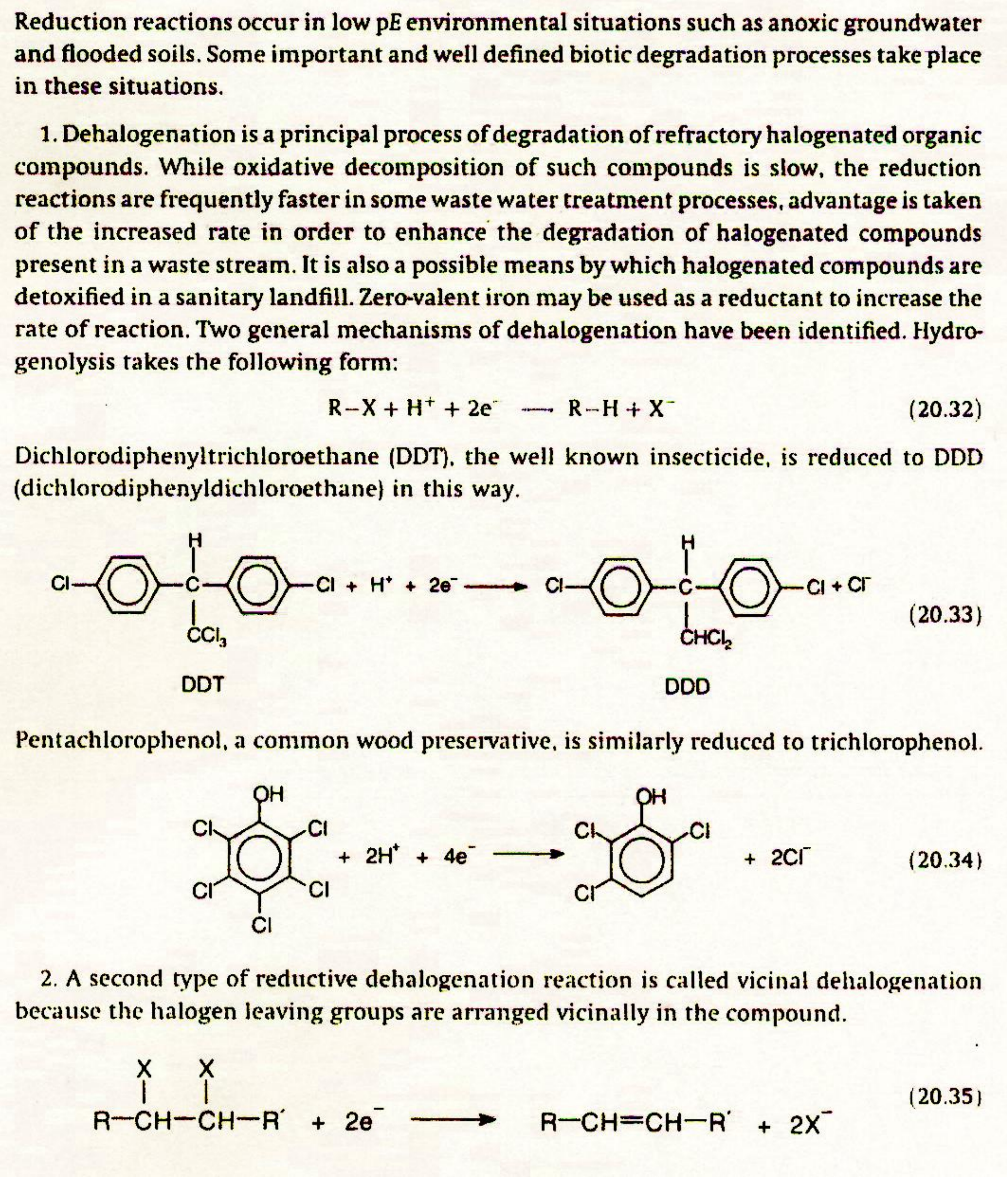
20.1 Chemical Stability: non-photolytic reaction

Reduction



Reduction reactions occur in low pE environmental situations such as anoxic groundwater and flooded soils. Some important and well defined biotic degradation processes take place in these situations.

1. Dehalogenation is a principal process of degradation of refractory halogenated organic compounds. While oxidative decomposition of such compounds is slow, the reduction reactions are frequently faster in some waste water treatment processes, advantage is taken of the increased rate in order to enhance the degradation of halogenated compounds present in a waste stream. It is also a possible means by which halogenated compounds are detoxified in a sanitary landfill. Zero-valent iron may be used as a reductant to increase the rate of reaction. Two general mechanisms of dehalogenation have been identified. Hydrogenolysis takes the following form:

$$R-X + H^+ + 2e^- \longrightarrow R-H + X^- \qquad (20.32)$$

Dichlorodiphenyltrichloroethane (DDT), the well known insecticide, is reduced to DDD (dichlorodiphenyldichloroethane) in this way.

(20.33)

Pentachlorophenol, a common wood preservative, is similarly reduced to trichlorophenol.

(20.34)

2. A second type of reductive dehalogenation reaction is called vicinal dehalogenation because the halogen leaving groups are arranged vicinally in the compound.

$$R-\overset{X}{\overset{|}{C}H}-\overset{X}{\overset{|}{C}H}-R' + 2e^- \longrightarrow R-CH=CH-R' + 2X^- \qquad (20.35)$$

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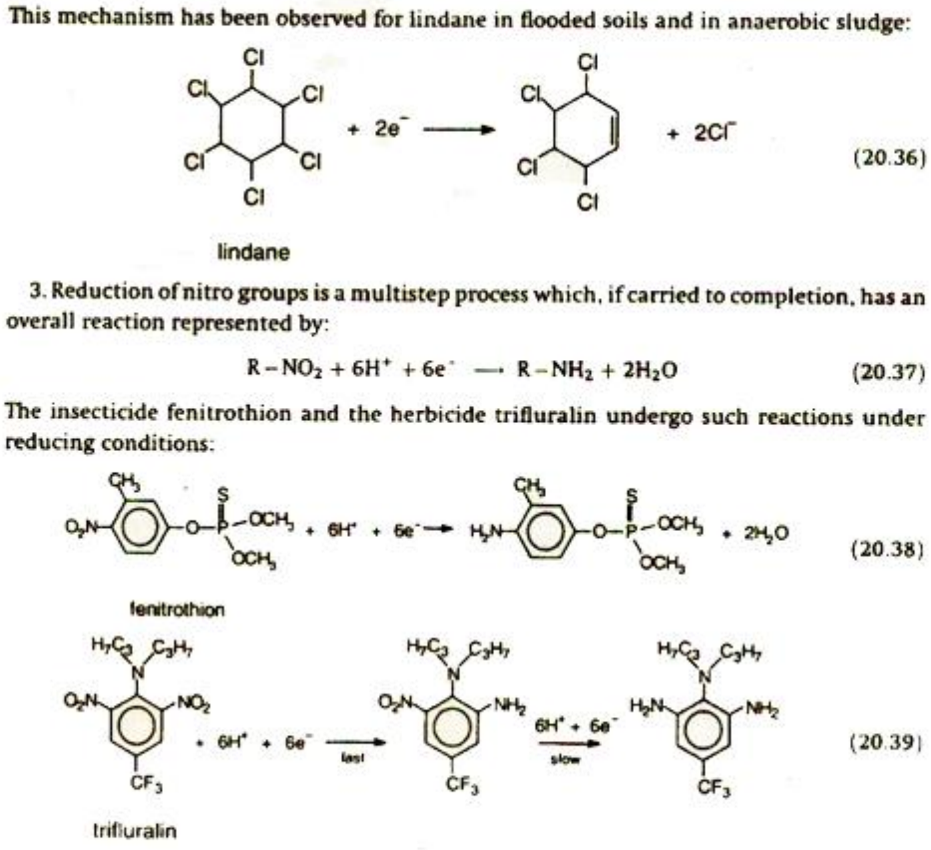
20.1 Chemical Stability: non-photolytic reaction

Reduction



This mechanism has been observed for lindane in flooded soils and in anaerobic sludge:

(20.36)

lindane

3. Reduction of nitro groups is a multistep process which, if carried to completion, has an overall reaction represented by:

$$R-NO_2 + 6H^+ + 6e^- \longrightarrow R-NH_2 + 2H_2O \qquad (20.37)$$

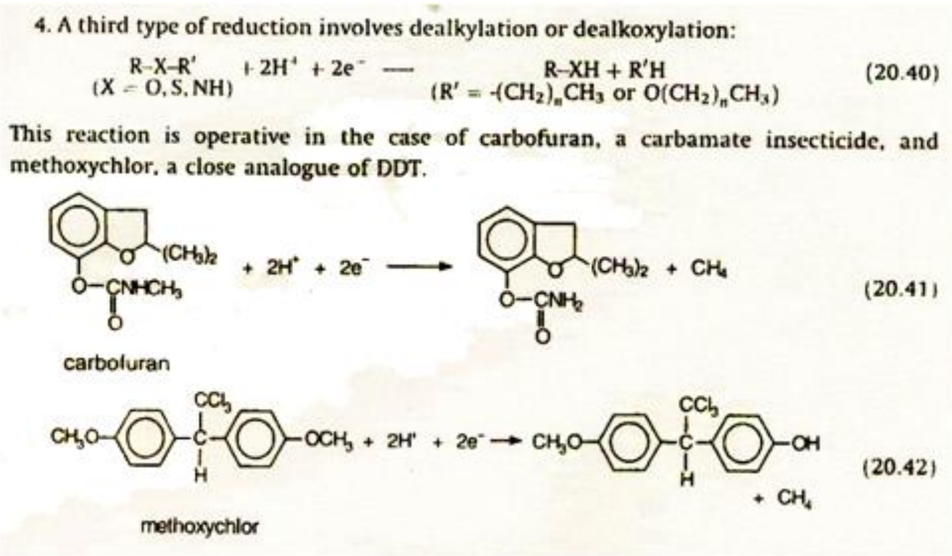
The insecticide fenitrothion and the herbicide trifluralin undergo such reactions under reducing conditions:

(20.38)

fenitrothion

(20.39)

trifluralin



4. A third type of reduction involves dealkylation or dealkoxylation:

$$\underset{(X = O, S, NH)}{R{-}X{-}R'} + 2H^+ + 2e^- \longrightarrow \underset{(R' = -(CH_2)_nCH_3 \text{ or } O(CH_2)_nCH_3)}{R{-}XH + R'H} \qquad (20.40)$$

This reaction is operative in the case of carbofuran, a carbamate insecticide, and methoxychlor, a close analogue of DDT.

(20.41)

carbofuran

(20.42)

methoxychlor

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20.1 Chemical Stability: Rates of degradative reactions

- Factors influencing the reaction rate
  1) Nature of the biocide:

Table 20.3 Persistence of pesticides in the environment

Pesticide class	Persistence ($t_{3/4}$)/months
Chlorinated hydrocarbons	16->24
Urea, trazine	3->18
Benzoic acid, amide	3-12
Phenoxy, toluidine, nitrile	1-6
Organophosphorus	0.2-3
Carbamate, aliphatic acid	0.5-3

From Edwards C.A., Persistent pesticides in the environment, 2nd edn, CRC press, Cleveland; 1973.

The $t_{3/4}$ value is the time taken for 75% of the pesticide to degrade in the field.

2) Temperature

3) Moisture

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20.1 Chemical Stability: Rates of degradative reactions

- Factors influencing the reaction rate

4) Soil/water properties

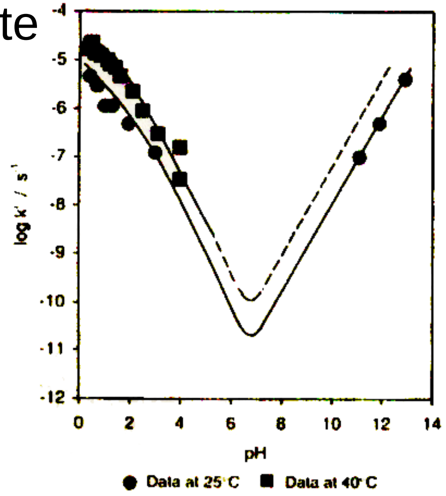
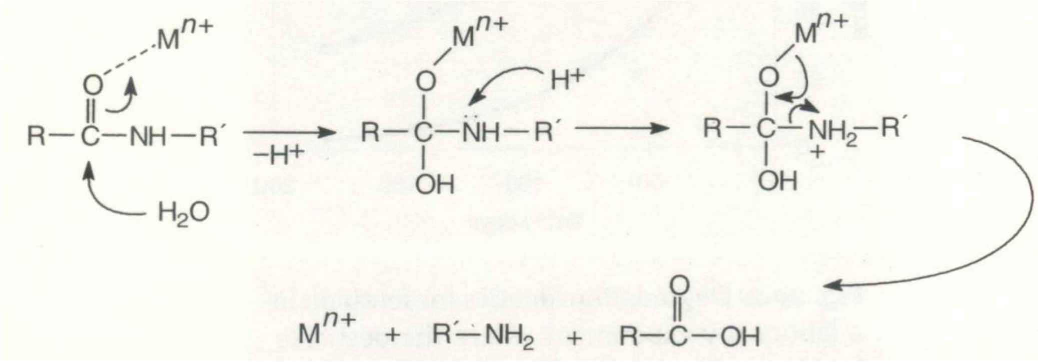


Fig. 20.1 The pH/rate constant profile for the triazine pesticide, atrazine. The figure is redrawn from some of the experimental and interpolated data provided in Plust, S.J., Loehe, J.R., Feher, F.J., Benedict, J.H., and Herbrandson, H.F., *J. Org. Chem.*, **46**, 3661–3665 (1981).

5) Soil/water properties

6) Soil/water properties



(20.43)

Chapter 20. Organic Biocides

20.1 Chemical Stability: Kinetic calculations

- E.g. degradation of fenthion – the first order rxn

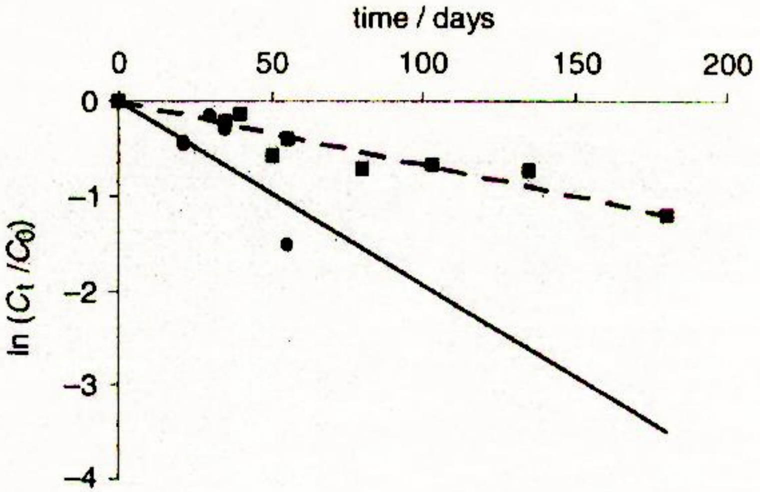
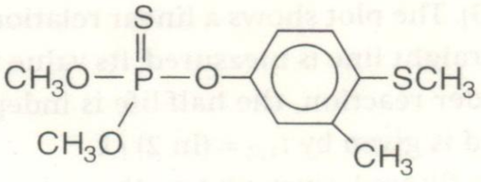


Fig. 20.3 Kinetic plot for the degradation of fenthion at (filled squares) 6 °C and 22 °C (filled circles). The slopes of the lines are -0.0066 days^{-1} (R^2=0.882) and -0.00194 days^{-1} (R^2=0.632) respectively.



fenthion