CHAPTER 2

Abiotic Processes

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2.1. PHYSICAL PROCESSES

When considering the effects of industrial chemicals in the environment, physical-chemical processes have a special importance since they are responsible, first, for the dispersion and, second, for the chemical changes which occur under abiotic conditions. The significance of biotic processes has, at times, been overemphasized, since degradation by this pathway is often quantitatively a minor factor by comparison with the physical-chemical processes.

The importance of abiotic degradation under atmospheric conditions has to be emphasized. In the past, research has been focused on the photochemical changes and degradation of organic chemicals, including investigations of the reaction mechanisms and the kinetics of such reactions. These studies involved laboratory experiments that did not attempt to simulate actual atmospheric conditions. It has been known for a long time that organic molecules are subject to isomerization, conversion, and incomplete degradation reactions through ultraviolet irradiation. It has not generally been recognized that mineralization* may take place even in

*As used in this section 'mineralization' means the complete degradation of organic compounds to inorganic products, e.g. carbonates and chlorides.
diffuse daylight. So far, only some organic chemicals such as methane, propane, and unsubstituted arenes which participate in the formation of the so-called photochemical smog, have been studied in great detail. The studies by Gäb et al. (1974a,b) demonstrate that even persistent chemical substances (e.g. photodieldrin) can be mineralized within relatively short periods if irradiated with light of wavelengths between 230 and 300 nm, as well as above 300 nm, the latter being a wavelength found in diffuse daylight.

Considering the fact that an instant availability of energy exists in the atmosphere, the abiotic (photochemical) degradation is probably a more important process than biodegradation which, in most cases, only leads to conversion products easily excreted by the living organism. Therefore, the atmosphere can be regarded as a large sink for persistent organic chemicals. Comparative studies of today’s global concentrations of some persistent chemicals such as DDT and dieldrin and the total amounts released suggest that the bulk may be mineralized.

Moreover it may be possible to estimate permissible emission levels by determining the rates of photochemical mineralization reactions in the atmosphere.

(i) Local, Regional, and Global Transport of Chemicals

The mechanisms leading to global dispersion of industrial chemicals are to some extent complex and can only be described approximately by scientific methods. A good correlation is found between the dispersion of $^{90}$Sr from atmospheric atomic bomb tests and the dispersion of DDT, where in both cases higher concentrations are present in the northern hemisphere. In order to achieve a better understanding of the transport phenomena, the differences between the local, regional, and global transport possibilities should be mentioned. Local transport mechanisms include those that change the environmental quality within a limited area intentionally, as in the case of pesticides and fertilizers. The pathways of these substances leading to the contamination of food are depicted in Figure 2.1.

Regional and global transport mechanisms involve an undesired dispersion of chemicals outside the area being treated, which leads to an occurrence of the corresponding chemicals in the global system. Although it is of greater importance for the understanding of the dispersion of industrial chemicals to deal with transport phenomena within the troposphere, the required three-dimensional models (which simulate the troposphere) can only be developed with great difficulties. For this reason, there are to date no satisfactory calculations for the lower atmosphere. The results of the model reported in the works of Pressman and Warneck (1970) and Bolin et al. (1963, 1970) seem to be better suited to the treatment of this problem by categorizing the dispersion mechanisms of the troposphere into vertical, longitudinal, intrahemispherical and interhemispherical transport pathways. The relevant references for these four aspects of transport are listed below.
Figure 2.1  Fates of chemicals in the environment

(a) Vertical and longitudinal mixing:
    Jakobi and Andre (1963)
    Junge (1962)
    Kroenig and Ney (1962)
    Lettau (1951)

(b) Intrahemispherical and interhemispherical mixing:
    Junge (1962)
    Lal and Rama (1966)
    Levy (1974)
    Nydal (1968)

(c) Troposphere — stratosphere exchange:
    Junge (1962)
    Pressman and Warneck (1970)
    Reiter et al. (1967)
    Smith (1968)
(ii) **Leaching of Ions and Organic Compounds in Soil and Landfills**

In the case of the washing out of organic compounds from the ground, the affinity of the soil for the chemicals must be considered. In general, and as expected, polar organic compounds adsorbed onto the soil can be more easily washed out than non-polar compounds. Therefore the classes of substances have increasing affinities in the following order: hydrocarbons < ethers < tertiary amines < nitro compounds < esters < ketones < aldehydes < amides < alcohols < acids.

The behaviour of pesticides serves as a practical example. It has been found experimentally that the affinity for the soil depends mainly on the structure of the chemical in question, on the physical properties of the soil, and finally on the chemical composition of the soil.

Transport phenomena are also strongly influenced by the accumulation of detergents or inorganic salts in the soil. Lichtenstein and Schultz (1965) have reported on these effects and have attempted to correlate the results of laboratory experiments with phenomena occurring in natural soils. The experiments with non-polar substances such as cyclodiene insecticides seem to verify the significance of these adsorption effects.

Due to their low water solubility, the insecticides aldrin and dieldrin are not transported deeply into the soil and do not enter into the ground-water. Recent studies show however, that after treating a 10 cm deep soil layer with $^{14}$C-aldrin, small amounts of aldrin, dieldrin, and photodieldrin penetrate up to 60 cm into the ground but that some degradation products are so strongly adsorbed that they cannot be extracted by organic solvents. The main product is dihydrochlorodendicarboxylic acid, which occurs at a depth of 60 cm in ground-water in concentrations as high as 0.05 ppm (Moza et al., 1972).

(iii) **Evaporation of Organic Chemicals from Soil and Surface Waters**

The removal of organic chemicals from soil is mainly dependent on the physical properties of the lower troposphere. Such factors as wind erosion and air extraction resulting from various types of air currents or soil agitation caused by living organisms and urbanization have a significant influence on the evaporation of organic chemicals from the soil. Organochlorine insecticides, such as dieldrin and heptachlor, have been shown to volatilize from soil into the atmosphere under field conditions. Five months after incorporation of these insecticides into the soil, 2.8 and 3.9%, respectively, had volatilized into the air (Caro et al., 1971). Studies carried out in the laboratory indicate that soil-incorporated residues of chlordane volatilize at a rate faster than that of dieldrin. Thus it would be expected that part of the chlordane applied to soil would be released into air, although the degree of volatilization would depend on the type of soil, soil moisture content, and weather conditions (Edwards, 1966). In the case of evaporation from surface water, physical
and mathematical methods are often employed since the entire process can be formulated as a type of steam distillation.

Generally, if two components are insoluble in each other (e.g. water and non-polar organic compounds), then each does not influence the vapour pressure of the other. Therefore, the total vapour pressure of a heterogeneous mixture is simply the sum of the vapour pressures of its individual constituents. Since the total vapour pressure is higher than the vapour pressure of the individual constituents, the boiling point of such a mixture must be lower than that of its lowest boiling constituent. This phenomenon takes place also for very dilute solutions of organic substances in water, since the composition of the distillate is independent of the absolute amount of the components.

(iv) Atmospheric Washout of Organic Chemicals

When considering the washout of organic chemicals in the atmosphere one of the main problems is to determine in what form the organic substances occur. The question of whether they exist in a gas phase, are adsorbed on solid or liquid aerosols or exist as clusters in the troposphere has been answered only for some chemicals. Previous work has generally been limited to the washout of radioactive particles and aerosols and it has been estimated that these particles have a lifetime of approximately 10 days (Francis et al., 1970) although some authors have reported lifetimes ranging from 20 to 50 days. It should be noted that rainout and washout usually occur in only the lowest 5 km of the troposphere.

(v) Dry Deposition from the Atmosphere

Although very little information is available on dry deposition, it could in some cases lead to the deposition of amounts comparable with those resulting from wet deposition.

(vi) Sedimentation of Organic Chemicals

Sedimentation of organic chemicals is especially noticeable in calm-water bodies where the process is often indirect, since organic chemicals are introduced attached to solid aerosols. Although there are a few reports of the sedimentation of organic chemicals in flowing waters, not much is known of the process or mechanisms.

Large amounts of chlordane residues were found in the sediments of the lower Mississippi River and several of its tributaries (Barthel et al., 1969). Thus, 0.12 to 1.28 mg/kg (dry weight) of chlordane residues were found in the mud samples from Wolf River/ Cypress Creek in Memphis, Tennessee. The high levels were attributed to a manufacturing operation in Memphis (highest levels were found at the factory site). Chlordane residues of 0.25 to 1.55 mg/kg of sample (dry weight) were found in sediments near formulating plants in Mississippi. Agricultural use of pesticides was not regarded as a significant contributor to the pollution of these waterways.
2.2. CHEMICAL PROCESSES

The abiotic changes which environmental chemicals undergo in nature can be classified into two groups, depending on whether or not ultraviolet irradiation from the sun occurs. The processes occurring in the absence of ultraviolet irradiation are limited to sedimentation by complexing with inorganic chemicals, hydrolysis and oxidation of organic chemicals.

(i) Sedimentation of Inorganic Chemicals

Sedimentation of inorganic chemicals by the formation of complexes with organic or inorganic compounds and pH-dependent equilibrium reactions all fall into this category. Accumulations of metals in river and sea sediments can also be included here, since they depend on the chemical and physical composition of the water. The precipitation reactions and pH dependence of equilibrium reactions have been reported in numerous publications. Although of interest, there have been few investigations on the sedimentation processes of biologically important metals such as mercury in rivers and the ocean.

Hasselrot (1968) found 34–168 ng/g (dry weight) of mercury in river sediments upstream of factories using mercury. Downstream of a paperboard mill using a mercurial fungicide the sediment was found to contain 18,400 ng/g at 1.6 km, 4,300–10,100 ng/g at 5 km, and 3,500–8,000 ng/g at 7 km, mostly in the upper 2 cm of sediment. Similarly, below a chloralkali plant, he found 11,600–26,000 ng/g in the upper 4 cm of sediment 550 m downstream and 1,200 ng/g in the top 1 cm of sediment 750 m downstream. Even 7 km downstream 440 ng/g were found. Similar analyses have been reported from the United States where contaminated sediments below a chloralkali plant contained 5,400–86,000 ng/g. Other areas, less contaminated, contained 600–4,000 ng/g (Anon, 1970). Saito (1967) reported 350–3,730 ng/g in river muds near Japanese industrial plants (processes unspecified), the overlying water generally having less than 10 ng/g.

Marine sediments near the Swedish and Japanese coasts have been examined. Sediments sampled in the sound between Denmark and Sweden, adjacent to the Swedish coast, were found to contain high mercury levels, up to 2,000 ng/g (dry weight), apparently due to pollution (Ackefors et al., 1970). Other marine sediments examined near the Swedish coast contained 1,000–1,500 ng/g. Sediments in the region of the discharge of mercury-containing effluents in Minamata Bay, Japan, were found to contain from 7,160–801,000 ng/g (Saito, 1967).

(ii) Hydrolysis of Organic Chemicals

It is known that many pesticides lose their toxic properties through hydrolysis in the environment; thus the reactivity of a pesticide in aqueous solutions can be used as an important criterion for its ecotoxicological behaviour.
Abiotic Processes

In Table 2.1 (Steller et al., 1960), the half-times of persistence of several phospho compounds is presented, where the half-time is the time required for a pesticide in aqueous solution to be degraded to one half its original concentration. It can be seen that the stability of all the chemicals rapidly decreases with increasing temperature. Stability also decreases with extremes of pH. Hydrolysis is also an important fate for chlorinated hydrocarbons. Heptachlor in aqueous solution is hydrolysed to hydroxychlordene, in which only the exo isomer is formed (Parlar et al., 1975a).

(iii) Oxidations

Oxygen can react with certain organic compounds, giving a hydroperoxide

\[ \text{RH} + \text{O}_2 \rightarrow \text{ROOH} \]

These reactions, which can take place under natural conditions, are referred to as autooxidation, and have the following free-radical mechanism:

\[ \text{RH} \rightarrow \text{R}^* \]
\[ \text{R}^* + \cdot\text{O} - \cdot\text{O} \rightarrow \text{R} - \text{O} - \cdot\text{O} \]
\[ \text{R} - \text{O} - \cdot\text{O} + \text{HR} \rightarrow \text{R} - \text{O} - \text{OH} + \text{R}^* \]

The chain reaction is stopped (suppressed) by, for example, the reaction of the radical initiators ROO• or R• with each other, and accelerated by peroxides, u.v. irradiation from the sun, and traces of heavy metals. The reaction is autocatalytic, since peroxides are formed in the course of the reaction.

Table 2.1  Halflives ($t_{1/2}$) of Organophosphorus Compounds in Aqueous Solution.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>Days</td>
<td>Days</td>
<td>Days</td>
<td>Days</td>
<td>Days</td>
<td>Days</td>
<td>Days</td>
</tr>
<tr>
<td>Parathion</td>
<td>13,800</td>
<td>3,000</td>
<td>690</td>
<td>180</td>
<td>50</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>Methyl-parathion</td>
<td>3,600</td>
<td>760</td>
<td>175</td>
<td>45</td>
<td>12.5</td>
<td>4</td>
<td>1.3</td>
</tr>
<tr>
<td>Chlorthion</td>
<td>2,900</td>
<td>600</td>
<td>138</td>
<td>36</td>
<td>10</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Metasystox Rl</td>
<td>4,800</td>
<td>970</td>
<td>236</td>
<td>62</td>
<td>18</td>
<td>5</td>
<td>1.7</td>
</tr>
<tr>
<td>Disulfoton</td>
<td>23,200</td>
<td>4,830</td>
<td>1,110</td>
<td>290</td>
<td>78</td>
<td>24</td>
<td>8</td>
</tr>
<tr>
<td>Azinphosmethyl</td>
<td>5,200</td>
<td>1,070</td>
<td>240</td>
<td>62</td>
<td>18</td>
<td>5.5</td>
<td>2</td>
</tr>
<tr>
<td>Trichlorphon</td>
<td>11,600</td>
<td>2,400</td>
<td>526</td>
<td>140</td>
<td>41</td>
<td>11</td>
<td>3</td>
</tr>
</tbody>
</table>
Heavy metals have a catalytic effect on the reaction and are able to convert peroxides into radicals according to the following steps:

\[
\begin{align*}
\text{ROOH} + \text{Me}^+ & \rightarrow \text{RO}^+ + \text{OH}^- + \text{Me}^{2+} \\
\text{ROOH} + \text{Me}^{2+} & \rightarrow \text{ROO}^- + \text{H}^+ + \text{Me}^+
\end{align*}
\]

Due to its lower reactivity, the peroxide radical is selective, and attacks more reactive CH bonds.

It has long been known that such reactions occur in nature. They have been observed in the spoiling of oils and fats and in the ageing of rubber and other polyenes. In the case of pesticides, it is known that aldrin reacts with oxygen from the air to give dieldrin in small yields. The oxidation of P=S bonds (found in phosphoric acid insecticides) to P=O groups probably results from an autooxidation process.

(iv) Photochemically Induced Processes

The atmosphere can be considered as a large chemical reactor in which chemicals react under the influence of irradiation from the sun and of catalysts in the form of trace elements. The reaction steps involved consist of parallel, sequential, and competitive reactions. To determine the individual mechanisms, conditions must be developed which mimic the atmosphere and permit, at the same time, a clear interpretation of the results. In this case complications arise due to the various reactions which occur simultaneously. Another approach would be the investigation of individual reaction steps. This can be achieved for example by deactivating the more reactive primary compounds and isolating and characterizing the resulting products.

(a) Photochemical Smog

The characteristic symptoms of photochemical air pollution were first encountered in the mid 1940’s in Southern California. This type of ‘smog’ was characterized by the presence of organic compounds not found in the ‘London smog’, which consisted of SO\(_2\) and aerosols. Several years later, Haagen-Smit (1964) established that it was indeed a new kind of air pollution, caused by the action of u.v. light on the exhaust emitted by the motor vehicles in the Los Angeles Basin. Haagen-Smit demonstrated that a mixture of nitrogen oxides with gasoline or olefins in the presence of sunlight, reproduced the smog damage on crops and showed that ozone was produced when individual organics such as olefins, alcohols, paraffins, and carbonyl compounds were irradiated in the presence of nitrogen dioxide. The same results could be demonstrated by the irradiation of automobile exhaust mixed with NO\(_2\).

Experiments under laboratory conditions with a mixture of nitrogen oxides and propylene in ppm concentrations show that NO is rapidly converted to NO\(_2\).
Simultaneously, the olefin concentration decreases and acetaldehyde appears. When the nitrogen oxide concentration is low, peracetyl nitrate and ozone build up while the nitrogen dioxide and C\textsubscript{3}H\textsubscript{6} concentrations fall. The major light-absorbing compound in this mixture is NO\textsubscript{2}, which dissociates to NO and ground-state oxygen atoms, i.e.

\[ \text{NO}_2 \rightarrow \text{NO} + \text{O}^\cdot \]

In air this is rapidly followed by

\[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \]

where M is a ‘third body’. In the presence of C\textsubscript{3}H\textsubscript{6}:

\[ \text{O} + \text{C}_3\text{H}_6 \rightarrow \text{Products} \]

\[ \text{O}_3 + \text{C}_3\text{H}_6 \rightarrow \text{Products} \]

Table 2.2 gives typical rate constants for the reactions of ozone with some olefins and with other species present in polluted urban atmospheres (Pitts and Finlayson, 1975).

Using these rates and commonly encountered pollutant concentrations, one calculates that the only important losses of ozone occur by reaction with unsaturated compounds. The rapid reaction of ozone with NO (O\textsubscript{3} + NO → NO\textsubscript{2} + O\textsubscript{2}) is the reason that ozone does not begin to accumulate until the NO concentration has decreased to a low value.

\( (b) \text{ Reactions of Organic Compounds with Active Oxygen} \)

Table 2.3 gives the values of selected rate constants for the reactions of O(\textsuperscript{3}P) with some olefins and arenes (Pitts and Finlayson, 1975). These rates, which show...
Table 2.3  Rate Constants for the Reactions of Oxygen \([O(\text{3P})]\) with Olefins. (Reproduced by permission of Verlag Chemie, Weinheim, Germany from Pitts and Finlayson, 1975)

<table>
<thead>
<tr>
<th>Olefin</th>
<th>(k \times 10^{-8})</th>
<th>Arene</th>
<th>(k \times 10^{-8})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1 mol(^{-1}) s(^{-1}))</td>
<td></td>
<td>(1 mol(^{-1}) s(^{-1}))</td>
</tr>
<tr>
<td>Ethylene</td>
<td>4.3 ± 0.5</td>
<td>Benzene</td>
<td>0.144 ± 0.02</td>
</tr>
<tr>
<td>Propylene</td>
<td>20 ± 1.7</td>
<td>Toluene</td>
<td>0.45 ± 0.045</td>
</tr>
<tr>
<td>1-Butene</td>
<td>24 ± 3.7</td>
<td>o-Xylene</td>
<td>1.05 ± 1.11</td>
</tr>
<tr>
<td>(\text{cis}-2)-Butene</td>
<td>92 ± 15</td>
<td>(m)-Xylene</td>
<td>2.12 ± 0.21</td>
</tr>
<tr>
<td>2-Methyl-2-butene</td>
<td>313 ± 30</td>
<td>(p)-Xylene</td>
<td>1.09 ± 0.11</td>
</tr>
<tr>
<td>2,3-Dimethylbutene</td>
<td>425 ± 46</td>
<td>1,2,3-Trimethylbenzene</td>
<td>6.9 ± 0.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,2,4-Trimethylbenzene</td>
<td>6.0 ± 0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,3,5-Trimethylbenzene</td>
<td>16.8 ± 2.0</td>
</tr>
</tbody>
</table>

An electrophilic trend, represent addition to the double bond. While it was suggested that abstraction may occur 15% of the time at 300°K in the \(O(\text{3P})-1\)-butene reaction, \(\cdot\text{OH}\) was not detected as an intermediate in this reaction, supporting previous assumptions that hydrogen abstraction is too slow to compete with addition at room temperature.

The model environmental chemicals aldrin (I), chlordene (II), and 2,2′-dichlorobiphenyl (III) react with \(O(\text{3P})\) to give oxygenated compounds (Saravanja-Bozanic et al., 1977), as shown in Figure 2.2.

(c) Reactions of Singlet Molecular Oxygen (Pitts, 1969)

It is known that the photooxygenation reactions of chemicals in photochemical smog fall into two groups: (a) those in which the photoexcited sensitizer molecule interacts directly with the substrate to produce free-radical species which react with the ground-state molecular oxygen present to give products, and (b) those in which the excited sensitizer transfers its energy to molecular oxygen producing singlet molecular oxygen, which in turn reacts with the substrate to give oxygenated products.

Briefly, the photosensitized oxidation by singlet oxygen involves the following sequence of reactions: it is now known to be general for gas-phase systems.

\[
\begin{align*}
\text{Absorption} & : \text{Sens} (S_0) + h\nu \rightarrow \text{Sens} (S_1) \\
\text{Intersystem} & : \text{Sens} (S_1) \rightarrow \text{Sens} (T_1) \\
\text{Energy} & : \text{Sens} (T_1) + ^3O_2 \rightarrow \text{Sens} (S_0) + ^1O_2 \\
\text{Chemical} & : ^1O_2 + \text{Acceptor} \rightarrow \text{Product}
\end{align*}
\]
There are two general reactions of $^{1}O_{2}$ with organic compounds:

1. The oxygenation of olefins containing allylic hydrogen atoms resulting in the shift of the double bond and formation of an allylic hydroperoxide; this is analogous to the so-called 'ene' reaction.
(2) The oxygenation of polycyclic aromatic hydrocarbons such as cyclopentadienes and heterocycles which give endoperoxides; this is analogous to the Diels–Alder reaction (Figure 2.3).

Singlet molecular oxygen may also be formed in several reactions involving neutral oxygen atoms, molecular oxygen, and ozone, as well as reactions of other simple inorganic molecules. Many of these are important upper-atmosphere processes and some may be significant in the lower atmosphere.

(v) Photoreactions of Cyclodienes

The photoreactions of cyclodienes can be divided into six classes of reaction:

(a) photoisomerization by $\pi\sigma \rightarrow 2\sigma$ reaction
(b) photoisomerization by $2\pi \rightarrow 2\sigma$ reaction

(c) photoreversible and irreversible hydrogen transfer reactions

(d) dechlorination reactions

(e) photochemically induced radical reactions

(f) dimerization reactions.

\((a)\) Photoisomerization by $\pi\sigma \rightarrow 2\sigma$ Reactions

Cyclodiene insecticides contain a chlorinated double bond, which can be excited by light of wavelengths greater than 300 nm. By interaction with the methylene bridge in the non-chlorinated part of the molecule, the corresponding photoisomeric product can be formed by a $\pi\sigma \rightarrow 2\sigma$ reaction. The excited double bond abstracts the opposite H atom, whereby a new $\sigma$ bond is formed (bridging) (Figure 2.4).

It has been determined from the irradiation of these compounds in D$_6$-acetone, that deuterium is not incorporated into the corresponding isomerization product. The reaction is thus intramolecular (Fischler and Korte, 1969).

\((b)\) Photoisomerization by $2\pi \rightarrow 2\sigma$ Reaction

All cyclodiene derivatives possessing a double bond on the unchlorinated ring at the \textit{endo} position react according to this mechanism (Figure 2.5).

\[\text{Figure 2.4 Photoisomerization of aldrin and dieldrin. When sensitized, these reactions proceed almost quantitatively. However they can also be observed unsensitized in the solid and gas phases. (Reprinted with permission from \textit{Tetrahedron Letters}, 32, 2793–2796, Fischler, H. M., and Korte, F. Sensitized and unsensitized photoisomerization of cyclodiene insecticides. © 1969, Pergamon Press, Ltd.)}\]
(c) Hydrogen Transfer Reactions

Besides the $\pi\sigma \rightarrow 2\sigma$ reactions resulting from the irradiation of dihydrochlordene derivatives there are reversible and irreversible hydrogen shifts. This type of suprafacial shift to two hydrogen atoms is referred to as a synchronous reaction. In the case of an unconcerted process, the radical formed in the first step can either recombine to form a bridged alkane or transfer a second hydrogen atom to form another alkene. A reverse reaction forming the corresponding starting compound should also be expected (Figure 2.6).

It could be shown that, during sensitized irradiation of 4,5,6,7,8,8-hexachloro-2,3,3a,4,7,7a-hexahydro-4,7-methano-1H-indene-1,3-dicarboxylic acid dimethyl ester (1), intramolecular reversible hydrogen shifts are possible as well as the
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πσ → 2σ reactions typical for this class of substances. Irradiation of (1) at low temperatures showed that below -30°C (5) is the only photoproduct. The photoisomerization products (2), (3) and (4), which arise by a πσ → 2σ reaction only above -30°C suggest that the reaction proceeds through the biradical intermediates (2a), (3a), and (4a). The parent compound (1) and the photoisomerization products (2), (3) and (4) are obtained by irradiation of (5) (Parlar et al., 1975b) (Figure 2.7).

(d) Dechlorination Reactions

In protonated solvents as well as in the solid phase, cyclodienes are photochemically dechlorinated at the chlorinated double bond. It may be assumed that the dechlorination reactions proceed from the singlet state of the molecule. In contrast to the above described photoisomerization reactions, in this case an intermolecular reaction also occurs whereby, after the photolysis of the C–C1 compound, the abstraction of a nearby H· (from solvent) occurs (Parlar and Korte, 1973) (Figure 2.8).
Figure 2.8  Photodechlorination reaction of chlorinated methanoindene

(e) Photochemically Induced Radical Reactions

It is evident from the formation of higher chlorinated compounds that a Cl radical is formed, which can chlorinate the starting compound. Therefore, heptachlor and isoseptachlor are formed from the irradiation of chlordene (Parlar and Korte, 1972). The formation of α-, β-, and γ-chlordene probably results from the attack on chlordene by a chlorine radical at the unchlorinated double bond (Gab et al., 1975) (Figure 2.9).

(f) Dimerization Reactions

Chlordene derivatives with the structural requirement to undergo a $2\pi \rightarrow 2\sigma$ reaction react at wavelengths above 280 nm in concentrated solutions to give dimers. Experiments have shown that this reaction requires a lower activation energy than the intramolecular $2\pi \rightarrow 2\sigma$ reaction (Parlar and Korte, 1972).

(vi) Photoreactions of Some Chlorinated Compounds

(a) DDT

It was found that DDT in the vapour phase in the presence of a large excess of air is converted very slowly to 1,1-dichloro-2,2-bis(p-chlorophenyl)ethane (DDD) and about 15 times more rapidly to 1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene (DDE) by ultraviolet light with wavelength 290–310 nm. DDD is stable to further
irradiation, but additional breakdown products are derived from DDE by the action of the ultraviolet radiation. In this case, 4,4'-dichlorobenzophenone (DDCO) and the intermediate 1-chloro-2,2-bis(p-chlorophenyl)ethylene (DDMU) are formed. DDCO is relatively stable to ultraviolet light. It has been shown, however, that it is transformed at a finite rate into 4,4'-dichlorobiphenyl (Maugh, 1973). Because all biphenyls are resistant to further irradiation in the vapour phase, one could expect that they should accumulate in the biosphere. This may in part explain the wide distribution of the PCBs which has been demonstrated in isolated areas far from the regions of original application.

(b) PCBs (Hustert and Korte, 1972, 1974)

The abiotic degradation of polychlorinated biphenyls was investigated using ultraviolet light of various wavelengths. In such experiments with 2,2', 4,4', 6,6'-hexachlorobiphenyl in non-polar solvents, a step-wise displacement of chlorine atoms, with the final production of unsubstituted biphenyl, could be demonstrated. Polymerizations and isomerizations are possible side reactions. In polar solvents, oxygen-containing compounds are also formed, for example, hydroxylated products. It is possible that the extremely toxic polychlorodibenzofurans, which have been detected as impurities in various industrial products, are also formed. Irradiation in the solid or liquid phase without solvent produces higher chlorinated products such as hepta- or octachlorobiphenyl.

(c) Dieldrin

During irradiation of dieldrin in solution, adsorbed or in the gas phase, photodieldrin is produced. This substance was chosen for photolysis studies in order to determine the conditions that cause a complete decomposition (mineralization) because it has up to now been considered to be one of the most persistent chemicals under normal atmospheric conditions.

During irradiation of adsorbed photodieldrin with light of wavelengths greater than 300 nm, photoaldrin-chlorhydrin and both photoaldrin ketone isomers could be isolated in pure condition. Besides these compounds, a mixture of substances, which could be separated by gas chromatography, was isolated in small yield. It was found that during chromatography compounds of lower chlorine content and low molecular weight developed. Parallel to these fragmentation products, however, higher molecular products may also be formed (Gäb et al., 1974a).

Irradiation of photodieldrin adsorbed on silica gel with wavelengths below 300 nm showed that more than 70% of the applied photodieldrin was changed under such conditions. Besides photoaldrin-chlorhydrin, the same products were identified as those which develop during adsorbed irradiation. These irradiations show that photodieldrin loses HCl in a primary step which is responsible for the opening of the epoxide ring.
Principles of Ecotoxicology

Table 2.4 Photodegradation of Photodieldrin. (Reprinted with permission from Chemosphere, 3(5), Gäb, S., Parlar, H., and Korte, F., Ecological chemistry. LXXXII. Ultraviolet-irradiation reactions of photodieldrin as a solid on glass and adsorbed to silica gel. © 1974, Pergamon Press, Ltd.)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield (mg)</th>
<th>Mass number</th>
<th>Number of Cl Atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photodieldrin</td>
<td>130</td>
<td>378</td>
<td>6</td>
</tr>
<tr>
<td>Photoaldrinchlorhydrin</td>
<td>140</td>
<td>414</td>
<td>7</td>
</tr>
<tr>
<td>Photoaldrin ketone I</td>
<td>45</td>
<td>378</td>
<td>6</td>
</tr>
<tr>
<td>Photoaldrin ketone II</td>
<td>25</td>
<td>378</td>
<td>6</td>
</tr>
<tr>
<td>I*</td>
<td>5</td>
<td>398</td>
<td>7</td>
</tr>
<tr>
<td>II</td>
<td>5</td>
<td>358</td>
<td>6</td>
</tr>
<tr>
<td>III</td>
<td>5</td>
<td>352</td>
<td>6</td>
</tr>
<tr>
<td>IV</td>
<td>10</td>
<td>432</td>
<td>8</td>
</tr>
<tr>
<td>V</td>
<td>5</td>
<td>344</td>
<td>5</td>
</tr>
<tr>
<td>VI</td>
<td>5</td>
<td>310</td>
<td>4</td>
</tr>
<tr>
<td>VII</td>
<td>5</td>
<td>324</td>
<td>4</td>
</tr>
<tr>
<td>VIII</td>
<td>5</td>
<td>294</td>
<td>3</td>
</tr>
<tr>
<td>IX</td>
<td>10</td>
<td>270</td>
<td>3</td>
</tr>
</tbody>
</table>

*Compounds I–IX are photoproducts which could not be identified by spectroscopic methods.

Irradiation of adsorbed photodieldrin in an oxygen stream with wavelengths below 300 nm revealed up to 95% degradation of photodieldrin to CO₂ and HCl.

Tests in the gas phase, however, revealed that isomeric photodieldrin is produced in large yield. This can be explained by a much longer duration of the electronically stimulated state of the dieldrin molecule in the gas phase. These conditions produce a larger yield from the bridging reaction which is favoured in comparison to the bimolecular reactions with oxygen species. Tests with pure ozone produced a hydroxy product in smaller quantities. Irradiation of adsorbed dieldrin in an oxygen stream at wavelengths below 300 nm revealed that dieldrin is almost quantitatively degraded to CO₂ and HCl. Small amounts of photodieldrin were found as well.

(d) Various Chlorinated Aromatics

The photochemical behaviour of hexachlorobenzene, pentachlorobenzene, pentachlorophenol, 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (DDT), 1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene (DDE), 2,4,5,2',4',5'-hexachlorobiphenyl and 2,5,2',5'-tetrachlorobiphenyl was investigated in the presence of a large excess of oxygen exposed to u.v. light with wavelengths longer than 230 nm (quartz glass) as well as with wavelengths longer than 290 nm ('Pyrex' glass). It was observed that the conversion rates of the substances adsorbed on particulate matter were far
Table 2.5  Results of Ultraviolet Irradiation of Aromatic Xenobiotics as Solids in an Oxygen Stream

<table>
<thead>
<tr>
<th>Compound</th>
<th>Irradiation conditions</th>
<th>Initial solid material (mg)</th>
<th>Recovered solid material (mg)</th>
<th>Mineralization products</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4,5,2',4',5'-Hexachlorobiphenyl</td>
<td>Quartz (7 days)</td>
<td>73</td>
<td>36</td>
<td>53 mg 19 mg n.d.</td>
</tr>
<tr>
<td></td>
<td>'Pyrex' (7 days)</td>
<td>70</td>
<td>68</td>
<td>n.d. n.d. n.d.</td>
</tr>
<tr>
<td>2,5,2',5'-Tetrachlorobiphenyl</td>
<td>'Pyrex' (7 days)</td>
<td>101</td>
<td>99</td>
<td>n.d. n.d. n.d.</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>Quartz (2 days)</td>
<td>63</td>
<td>23</td>
<td>46 mg 13 mg 13 mg</td>
</tr>
<tr>
<td></td>
<td>'Pyrex' (7 days)</td>
<td>82</td>
<td>81</td>
<td>n.d. n.d. n.d.</td>
</tr>
<tr>
<td>Pentachlorobenzene</td>
<td>'Pyrex' (7 days)</td>
<td>64</td>
<td>62</td>
<td>n.d. n.d. n.d.</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>'Pyrex' (7 days)</td>
<td>80</td>
<td>69</td>
<td>13 mg 6 mg n.d.</td>
</tr>
<tr>
<td>DDT</td>
<td>'Pyrex' (7 days)</td>
<td>54</td>
<td>89</td>
<td>12 mg 2 mg n.d.</td>
</tr>
<tr>
<td>DDE</td>
<td>'Pyrex' (7 days)</td>
<td>98</td>
<td>85</td>
<td>10 mg 8 mg n.d.</td>
</tr>
</tbody>
</table>

n.d. = not detected.
higher than with those deposited as solids or thin films on a glass surface (Gab et al., 1974b).

These differences can be attributed to the bathochromic shift, changes in the relative extinction, or appearance of new absorption bands as a consequence of the adsorption on silica gel, as well as to the greater dispersion of pesticide molecules in the adsorbed phase resulting in a higher pesticide-oxygen contact. The disappearance of the applied substances can be explained neither by their vapour pressures nor by formation of photoproducts. Since CO₂ and HCl are formed during ‘Pyrex’ irradiation of pentachlorophenol, DDT and DDE as solids on glass and the u.v. absorption bands of these compounds are located in nearly the same region as those substances adsorbed on silica gel, it is evident that in this case mineralization products are evolved as well.

Ultraviolet irradiation of chlorinated olefins (e.g. vinyl chloride, dichloroethylene, trichloroethylene and tetrachloroethylene) in the presence of excess oxygen also results in products of low molecular weight such as CO₂, COCl₂, and HCl. The primary step of this photooxidation process is the formation of the respective epoxides. Irradiation of ethyl acetate and ethanol in the presence of NO₂, SO₂, and H₂O in concentrations which can be found in polluted areas resulted in a degradation of these compounds under simulated tropospheric conditions.

(vii) Evaluation of the Reactions of Organic Chemicals

(a) Significance of Dechlorination Reactions

Approximately 40% of insecticides contain chlorine, which is in most cases responsible for the efficiency and toxicity of the compound. A biological transformation or u.v. irradiation in the atmosphere can dechlorinate an environmental chemical, which often results in a loss of its toxicity.

Experiments have shown that a pesticide remains for only a relatively short time after application in a treated area and is quickly dispersed into the atmosphere. An understanding of the following factors is necessary to predict the rate of dechlorination in the atmosphere:

(a) The amount produced, the area treated, and the dispersion of environmental chemicals.
(b) Intensity of irradiation from the sun depending on the height in the atmosphere.
(c) Reactivity and reaction pathways after adsorption on surfaces (liquid and solid aerosols).
(d) Kinetics and quantum yields of the photochemical reactions of chemicals under simulated atmospheric conditions.
Table 2.6 Results of Ultraviolet Irradiation of Aromatic Xenobiotics Adsorbed on Silica Gel

<table>
<thead>
<tr>
<th>Compound</th>
<th>Initial quantity adsorbed&lt;sup&gt;a&lt;/sup&gt; (mg)</th>
<th>Quantity remaining adsorbed after 4 days' irradiation&lt;sup&gt;b&lt;/sup&gt; (mg)</th>
<th>Quantity remaining adsorbed after 7 days' irradiation&lt;sup&gt;c&lt;/sup&gt; (mg)</th>
<th>Photoproducts detected after 7 days' irradiation&lt;sup&gt;b, c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentachlorophenol</td>
<td>102 (100%)</td>
<td>24 (25%)</td>
<td>12 (12%)</td>
<td>None</td>
</tr>
<tr>
<td>DDT</td>
<td>185 (100%)</td>
<td>298 (77%)</td>
<td>255 (66%)</td>
<td>None</td>
</tr>
<tr>
<td>DDE</td>
<td>162 (100%)</td>
<td>91 (25%)</td>
<td>69 (19%)</td>
<td>Dichlorobenzophenone 38 mg; trichlorobenzophenone 7 mg</td>
</tr>
</tbody>
</table>

<sup>a</sup> In each case the substance was adsorbed on 100 g silica gel.

<sup>b</sup> Quantitation was by means of gas chromatography (BDC) and comparison with standard solutions of known concentration as well as by measurements of the u.v. extinction.

<sup>c</sup> The possibility that more polar compounds arise, which are not eluted under these conditions, and consequently are not detected, cannot be excluded.
Reported results provide sufficient information about the above-mentioned points, although comparative investigations with other classes of substance are still lacking.

(b) Significance of Photoisomerization Reactions

Photoisomerizations are specific reactions which have a lower activation energy in comparison to other photoreactions. For this reason it is important to investigate the toxic and ecotoxicological properties of the photoisomers formed as primary products under atmospheric conditions. All photoisomers of the cyclodiene are more toxic than the starting compounds. The extent of damage to the environment caused by these stable photoproducts, as well as their direct side effects, can be estimated by determining the lifetime under atmospheric conditions of the corresponding chemical.

(c) Significance of Photooxidation Reactions

The rearrangement of chemicals under atmospheric conditions is strongly dependent on the type of oxidants present during the reaction. For example, the oxygen molecule possesses two unpaired electrons in the ground state and is in the triplet state (\(^3\text{O}_2\)) and paramagnetic. Two electron configurations are possible for the excited singlet state of oxygen, the so-called \(^{1}\Delta g\) and \(^{1}\Sigma^g^+\) configurations, although their formation through the absorption of irradiation from the sun is not significant. In the case of widening of the lines of \text{O}_2 due to collisions, the excited singlet \text{O}_2\ (^{1}\Delta g) can be formed in such concentrations and be so long-lived as to react (favourably) with olefins and aromatic compounds in the atmosphere.

Oxygen molecules can also be converted into oxygen atoms by u.v. light of shorter wavelength. This process is found in the higher layers of the atmosphere (outside the troposphere).

Oxygen atoms in atmospheric layers near ground level are formed from the photodissociation of nitrogen dioxide in concentrations estimated at approximately \(10^{-8}\) ppm. Ozone also plays a special role here. It is therefore interesting in an ecological sense to study the reactions of environmental pollutants in the presence of \(\text{O}_2\), \(\text{O}_3\), \(\text{NO}_2\), \(\text{O}\), and \(\text{O}_2\ (^{1}\Delta g)\), which in many cases can be carried out under simulated conditions. These studies furnish necessary data for estimating the quality of the environment and information about the primary photoreactions leading to the buildup of smog.

(d) Significance of Photomineralization Processes

It has been shown that the irradiation of several chemically stable compounds (aldrin, dieldrin, chlordene, photodieldrin, hexa- and tetrachlorobiphenyl, hexachlorobenzene, pentachlorobenzene, DDT, and DDE) in their solid states and at
wavelengths smaller than 290 nm leads to a mineralization of those compounds into CO₂ and HCl. In the case of aldrin, dieldrin, DDT, DDE, and pentachlorophenol, photomineralization is also achieved at wavelengths greater than 290 nm. Similar results are found for the irradiation of these compounds when absorbed on silica gel. It can be concluded from the experiments that the u.v. irradiation from the sun possesses sufficient energy to decompose these stable compounds. A systematic study of other specific classes of compounds is needed to determine whether those reactions also apply to other environmental chemicals.

(viii) Laboratory Models for Testing Abiotic Degradability

In order to investigate the reactions of environmental chemicals under natural conditions, it is necessary to develop experimental conditions which correspond to atmospheric conditions. There are generally five types of reactions:

1. photochemical reactions of environmental chemicals in solution;
2. photoreaction of environmental chemicals on solids;
3. photoreactions of environmental chemicals in the gas phase;
4. photoreactions of environmental chemicals in the gas phase with other gases (e.g. NO₂, SO₂, O₃, O);
5. photocatalysed reaction of environmental chemicals in the gas phase at the surface of solid or liquid phases (this type of reaction simulates the reaction of chemicals on the surface of dust particles and on solid or liquid aerosols found in the atmosphere).

Standardized values have been found from these experiments which can be used as parameters in the evaluation of environmental chemicals.

2.3. REFERENCES


