

2.4 *Degradation in the Liquid and Adsorbed Phase*

H. PARLAR and D. KOTZIAS

*Gesellschaft für Strahlen- und Umweltforschung mbH, München
Institut für Ökologische Chemie
Schulstraße 10
D-8050 Freising-Attaching
Federal Republic of Germany*

2.4.1	Possible Photo-induced Reactions of Organic Compounds Under Natural Conditions	81
2.4.2	Determination of Environmental Photochemical Degradability of Organic Compounds in Liquid Phase	85
2.4.2.1	The significance of quantum yield during determination of photochemical degradability	85
2.4.3	Determination of Environmental Photochemical Degradability of Organic Compounds in the Solid and Adsorbed Phase	93
2.4.3.1	UV behaviour of environmental chemicals in the heterogeneous phase	95
2.4.3.2	Phototransformation of organic chemicals to inorganic products (photomineralization)	99
2.4.3.3	Photomineralization of freons	100
2.4.3.4	Efficiency of photomineralization experiments	102
2.4.4	Conclusions	104
2.4.5	References	104

2.4.1 POSSIBLE PHOTO-INDUCED REACTIONS OF ORGANIC COMPOUNDS UNDER NATURAL CONDITIONS

When considering the fate of an organic compound in the troposphere, independent of whether this substance is present in the gas, solid, or dissolved phase, if we assume that it cannot absorb UV light above 290 nm, then in theory only one type of reaction is possible. The reactive species in the troposphere (among them NO_2 , O_3 , $^1\text{O}_2$) can attack the molecule. Thus, if a compound fulfils the structural requisites it will undergo reactions with these species, leading to intermolecular products (Figure 2.4.1).

On the other hand, if the basic skeleton or the functional groups of the molecule, or the combination of the two make possible the absorption of UV

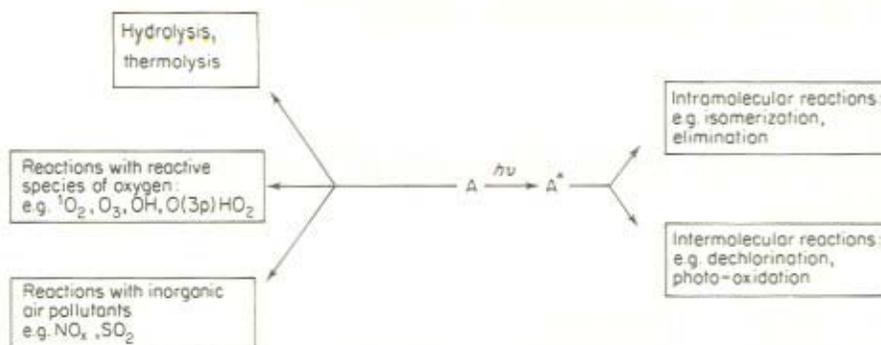


Figure 2.4.1 Possible reactions of environmental chemicals under abiotic conditions

radiation, then the following photophysical and photochemical steps may be anticipated: (a) Dipole transitions. (b) Radiation-free transition. (c) Energy transfer, itself divisible into two groups: (1) energy transfer by radiation, (2) radiation-free energy transfer (Figure 2.4.2) (Gäb, 1977; Parlar and Korte, 1977; Parlar, 1980).

The molecule becomes activated by absorption of a photon from a molecule with complete electron shells and is thus raised from the singlet ground state (S_{00}) to a higher electronic vibration level (S_{nL}) of equal multiplicity according to the selection rules (process 1). Transitions to an excited triplet state are also possible (process 2) but are seldom observed because the transitional moment is small. The reactions back to the lower-lying singlet state are called fluorescence (process 3) and phosphorescence (process 4). Fluorescence can also occur as a reaction emanating from a first triplet state T_{10} , where radiation-free transitions lead to the first singlet state.

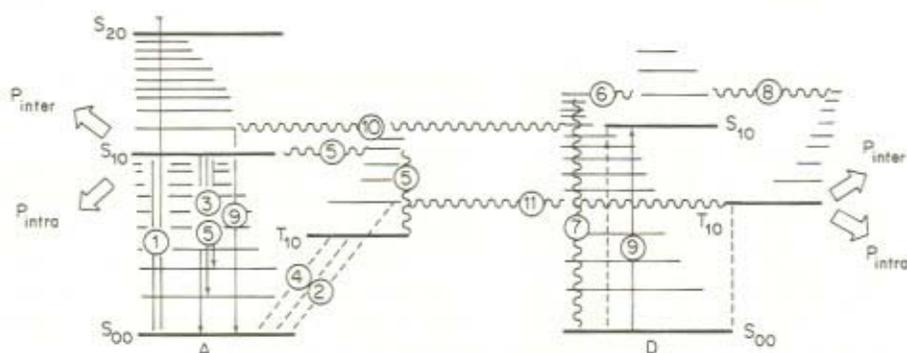


Figure 2.4.2 Possible photophysical and photochemical processes of an organic chemical.

Normal fluorescence then follows; the overall process is called delayed fluorescence (process 5).

The molecule can pass to the S_{00} state rapidly and without emitting radiation from the activated singlet state S_{01} . Such a radiation-free transition between states of equal multiplicity is called an 'internal conversion' (process 6). The original process occurs in two steps: the actual internal conversion, i.e. the transition from the activated singlet state (S_{11}) to a degenerate or quasidegenerate state (S_{01}), and a subsequent transition from S_{01} to S_{00} . This second step is called vibration relaxation (process 7).

The internal conversion, which can also occur between activated triplet states, is brought about by overlapping of the potential hypersurfaces of the two activated states. It is noteworthy that the rate constant of the reaction K_4 is 10^{12} sec^{-1} , and by contrast, the subsequent process takes place very slowly because of the small difference in energy.

The internal conversion process is the reason why especially condensed-phase chemical reactions occur mainly from first singlet or triplet levels (Kasha's Golden Rule). In addition condensed-phase deactivation processes are bimolecular in nature and are therefore diffusion-controlled. The activation for the further photochemical reaction energy is very small, because the molecule has received an excess of energy by absorption of a photon. Every collision of the partners produces a reaction; however, the velocity of the reaction is determined solely by the rate of diffusion of the reactants, which is a function of the temperature, viscosity and lifetime of the activated species.

During an internal conversion the radiation-free process takes place between states of equal multiplicity. When this change occurs between states of different multiplicity it is called intersystem crossing or spin-system change (process 8). Except for the reversal of spin this process is governed by the same mechanisms as is internal conversion.

Energy transfer, which plays a particularly important part in photochemical processes, can be divided into two groups:

- (1) Direct energy transfer (process 9) involving the return of an activated donor molecule to the ground state; the quantum liberated can activate an acceptor molecule. All that is required is that the emission spectrum of the donor molecule and the absorption spectrum of the acceptor molecule should possess as wide as possible an overlapping region. Energy transfer ensues by radiation because a photon always participates in the process.
- (2) Radiation-free energy transfer can occur either from a singlet-excited donor molecule involving singlet excitation of an acceptor molecule (process 10), or else a triplet-excited donor molecule in its turn transfers its energy to a triplet-state acceptor molecule (process 11).

Table 2.4.1 Reaction velocity constants of the reaction of aromatic hydrocarbons with OH radicals

Hydrocarbon	$10^{12}k \times \text{cm}^3 \times \text{mol}^{-1} \text{s}^{-1}$
Benzene	1.20 ± 0.15
Toluene	6.40 ± 0.64
<i>o</i> -Xylene	14.3 ± 1.5
<i>m</i> -Xylene	24.0 ± 2.5
<i>p</i> -Xylene	15.3 ± 1.7
1,2,3-Trimethylbenzene	33.3 ± 4.5
1,2,4-Trimethylbenzene	40.0 ± 4.5
1,3,5-Trimethylbenzene	62.4 ± 7.5

All processes ranking as photophysical transitions are processes which lead to no chemical change, but which are responsible for the individual component steps and reactions. They are simplified representations which make very complicated reaction modes more easily understood. A study of these processes enables the photo-transformations of industrial chemicals in the environment to be described photokinetically. In the majority of the cases, however, direct or indirect excitation of homogeneous-phase environmental chemicals is limited to certain substance classes. If the molecule is not excited in the troposphere, it can be attacked by reactive species existing there (among them $\cdot\text{OH}$, $\cdot\text{OOH}$, O_3). However, considering the lack of reactivity of stable environmental chemicals with these reactive species and their normal low concentration in the troposphere one may postulate that no appreciable degradation of such compounds can take place in either the gas or aqueous phase. These radicals, with the exception of the OH radical which reacts relatively rapidly with environmental chemicals in the gas phase, therefore play a minor part in the transformation of complex organic chemicals (Table 2.4.1).

Table 2.4.2 Contamination of highway dust with polycyclic hydrocarbons

Compound	$\mu\text{g}/\text{m}^2/\text{day}$		
	Winter	Spring	Summer
Pyrene	1.03	0.26	0.73
1,10-Benzofluoroanthene	1.44	0.19	1.17
Tetracene	0.86	0.20	0.52
Benzopyrene	1.84	0.77	1.22
Coronene	0.63	0.26	0.36
Dibenzopyrene	1.84	0.56	0.50
Rubicene	2.01	0.47	0.40
Fulminene	0.46	0.39	0.23

The prime requisite for defining a relevant sink for bioactive organic chemicals is to characterize their occurrence in different ecosystems, and notably in the atmosphere. Most of these compounds are present on solid and liquid aerosols in enriched form but seldom are found to occur in the gas phase (cf. Table 2.4.2) (Herlan, 1975).

2.4.2 DETERMINATION OF ENVIRONMENTAL PHOTOCHEMICAL DEGRADABILITY OF ORGANIC COMPOUNDS IN LIQUID PHASE

Three basic systems are potentially available for characterizing photochemical degradability of an organic compound in liquid phase:

- (a) *Behaviour under natural conditions*—A residue analysis after application or spill of the organic chemical is used to describe the behaviour of the compound in a particular and spatially limited ecosystem. A controlled investigation of the compound after a deliberate application to the ecosystem would be scientifically profitable, but, for understandable reasons, may be impossible to carry out or may be undertaken only in restricted circumstances.
- (b) *Behaviour under simulated environmental conditions*—Investigations can be carried out in different organic solutions and water systems, according to the physico-chemical properties of the compound.
- (c) *Photophysical behaviour*—An evaluation can be used to test the extent to which individual reaction steps are feasible, whether a reaction proceeds uniformly or whether intermediate stages occur.

All the techniques proposed have advantages and limitations. A satisfactory elucidation of the degradation process may require an appropriate combination of all methods, but the problem can be simplified if an assessment within a particular substance class is required. In such a case, structural features of individual compounds are first measured, and then, by employing suitable photophysical methods, a correlation between degradability and structure is attempted.

2.4.2.1 The significance of quantum yield during determination of photochemical degradability

The use of artificial light sources in simulation models can cause difficulties (Parlar *et al.*, 1982). Assume, for example, that a compound (A) has its UV maximum at wavelength x and another compound (B) has its maximum at wavelength y . Assume further, that the light source used has a favourable spectral distribution over the relevant UV regions, thus confronting compound A with a strong band at the wavelength x but not compound B at

wavelength γ . A comparison between these two substances is then impossible. For a valid comparable structure degradability correlation both substances A and B must receive radiation of equal intensity at their UV maxima. To provide comparable radiation for activation the use of monochromatic light is a necessity, and the number of absorbed quanta per unit time must be the same for both compounds. This condition is also a prerequisite for the further reactions of substances A and B. Whether these substances react further, and to what extent, will depend directly on their structures.

Quantum yield is defined as:

$$\Phi = \frac{\text{Number of molecules decomposed (or formed)}}{\text{Number of light quanta absorbed}}$$

Quantum yield is therefore a suitable kinetic variable for the development of correlations between photochemical stability in the environment and structural features of organic compounds. In the following section some investigations are described which demonstrate the importance of quantum yield.

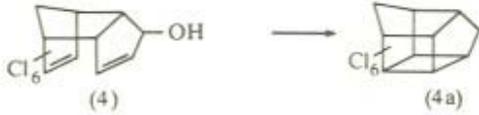
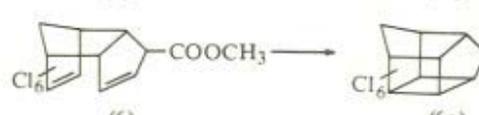
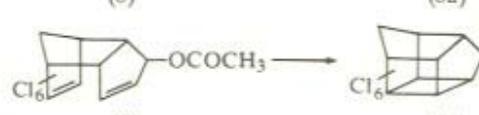
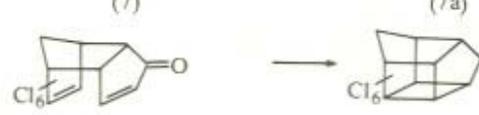
[2 + 2]-Cycloaddition of chlordene derivatives

A prime example of the use of the quantum yield concept in estimating reactivity is the photochemical [2 + 2]-cycloaddition of some chlordene derivatives. Solar UV radiation converts compounds 1–8 (Table 2.4.3) to their full-cage isomers, known to be more stable than the starting substances (Parlar, 1980). Table 2.4.3 shows the quantum yields of these reactions measured in dioxane-acetophenone at 20 °C using total absorption. A comparison of substance decomposition quantum yield (Φ_p) with [2 + 2]-photo-isomer formation quantum yield (Φ_i) shows large discrepancies in some of the reacting compounds (for instance 5 and 6) and indicates formation of alternative photoproducts.

Thus, the ratio Φ_i/Φ_p during the photochemical rearrangement $6 \rightarrow 6a$ was 16.470, during $4 \rightarrow 4a$ was 24.444 and during $5 \rightarrow 5a$ was 82.608. By contrast, the ratio found for the photochemical [2 + 2]-cycloaddition $8 \rightarrow 8$ was 1.068, indicating an almost complete absence of secondary product formation during this reaction. A comparison of the substance decomposition quantum yields reveals no great differences, with values of between 1.10 and 6.07×10^{-2} . Compound 7 was an exception as it did not react under these conditions.

The measured quantum yields of the photochemical [2 + 2]-cycloaddition of the chlordene derivatives indicate that these reactions in solution do not proceed according to a chain mechanism. Consequently, thermodynamic aspects can play only a subordinate role in these reactions. To determine the

Table 2.4.3 Quantum yields of [2 + 2]-cycloaddition of some chlrodene derivatives

Reaction	(Φ_p)	(Φ_r)	Φ_r/Φ_p
 (1) → (1a)	$2.35 \cdot 10^{-3}$	$4.90 \cdot 10^{-3}$	2.085
 (2) → (2a)	$2.41 \cdot 10^{-3}$	$5.12 \cdot 10^{-3}$	2.124
 (3) → (3a)	$2.27 \cdot 10^{-3}$	$6.07 \cdot 10^{-3}$	2.674
 (4) → (4a)	$4.50 \cdot 10^{-4}$	$1.10 \cdot 10^{-3}$	24.444
 (5) → (5a)	$0.46 \cdot 10^{-4}$	$3.81 \cdot 10^{-3}$	82.608
 (6) → (6a)	$1.70 \cdot 10^{-4}$	$2.80 \cdot 10^{-3}$	16.470
 (7) → (7a)	0	0	0
 (8) → (8a)	$2.34 \cdot 10^{-3}$	$2.50 \cdot 10^{-3}$	1.068

triplet energy of the starting compounds it is useful to measure the full-cage isomer formation quantum yields in the presence of typical triplet sensitizers.

In accordance with the equation,

$$K_{ET} \sim \frac{\Phi_r}{\tau_{sens} \Phi_{isc}^{sens}}$$

K_{ET} represents the energy frequency rate. It is therefore more appropriate to

plot the expression,

$$\frac{\Phi_T}{\tau_{\text{sens}} \Phi_{\text{isc}}^{\text{sens}}}$$

against the sensitizer triplet energy (E_T) as in Figure 2.4.3.

This figure readily shows that the triplet energy of the photochemical isomerization lies between 62.2 and 66.6 kcal/mol. In order to remove all doubt that a triplet reaction is involved, experiments with a suitable quencher are necessary. Plotting the reciprocal of quantum yield ($1/\Phi$) against the quencher concentration (Q) gives the so-called Stern-Vollmer diagram based

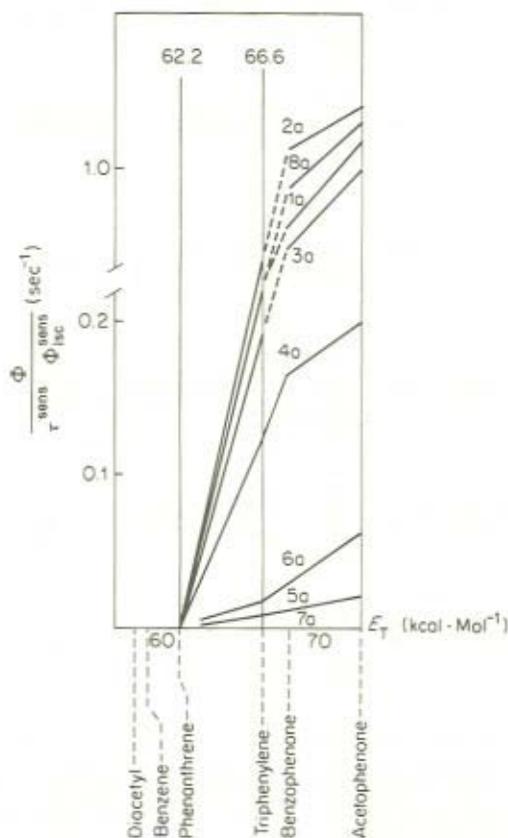


Figure 2.4.3 Energy frequency rate ($\Phi_T / \tau_{\text{sens}} \cdot \Phi_{\text{isc}}^{\text{sens}}$) of the full-cage isomer formation of some chlordene derivatives (1-8) in the presence of triplet sensitizers

on the following equation:

$$\frac{1}{\Phi} = \frac{K_r[T] + K_q[Q][T] + K_d[T]}{K_i[T]} = \frac{K_r + K_d}{K_i} + \frac{K_q}{K_i} Q$$

In this equation $[T]$ is the concentration of the activated triplet, $[Q]$ is the quencher concentration and K_d is the triplet deactivation rate constant. The equation follows from the definition of the quantum yield as the ratio of the rate at which a product is formed from the activated state to the rate of all reactions leading to a decrease in the activated molecule concentration. It means that $1/\Phi$ and Q are proportional to each other and that the slope of the straight line is equal to the triplet rearrangement rate constant (K_r). If the quenching reaction is diffusion-controlled, then K_q in the above equation can be replaced by the known diffusion rate constant, and K_r can be calculated from the slope.

Chlordene (1) was used as a model substance for these investigations. It is converted to the full-cage isomer (1a) even on direct irradiation ($\lambda = 277$ nm). *Trans*-piperylene ($E_T = 59$ kcal/mol) was used as a quencher (Figure 2.4.4).

Oxygen can participate in various ways during photochemical processes. Its ability to quench triplet states because of their long life produces a substantial, partial-pressure-related reduction in quantum yield in all photochemical reactions involving such states. Experiments of this type also provide important indications about the nature of the initial state.

During the photochemical reactions of chlordene derivatives 1 and 2, air was removed from the solvents by repeated freezing, evacuation and thawing,

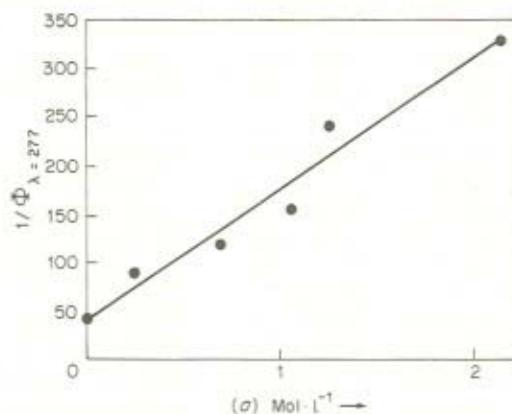


Figure 2.4.4 Stern-Vollmer diagram of the photoreaction chlordene (1) to photochlordene (1a)

Table 2.4.4 Quantum yields of the photochemical [2 + 2]-cycloaddition of chlordene compounds 1 and 2 as a function of oxygen partial pressure (in dioxane/acetophenone at 20 °C using total absorption)

Compound	pO_2	$2pO_2$	$4pO_2$
1	$1.72 \cdot 10^{-3}$	$2.01 \cdot 10^{-3}$	$2.35 \cdot 10^{-3}$
2	$1.80 \cdot 10^{-3}$	$2.00 \cdot 10^{-3}$	$2.41 \cdot 10^{-3}$

and replaced by inert gas. It was found that the reaction velocity increased as the oxygen partial pressure fell (Table 2.4.4).

These experiments show that:

- The [2 + 2]-photo-cycloadditions of the chlordene derivatives can be triplet-sensitised in solution,
- the cycloaddition in solution can be blocked with triplet quenchers,
- the triplet energy lies between 62.2 and 66.6 kcal/mol,
- the rate constant of the triplet rearrangement (K_t) is $1.4 \times 10^7 \text{ sec}^{-1}$.

Deamination of 4-amino-3-methylthio-1,2,4-triazine-5(4H)-ones (9-13)

The second example of the use of quantum yields involves the photo-induced deaminations of 4-amino-3-methylthio-1,2,4-triazine-5(4H)-ones (9-13) (Herrmann, 1982). These compounds are a new class of herbicides with an action based on the inhibition of photosynthesis. Extensive studies have led to a substantial understanding of the structural requisites for these Hill reaction inhibitors. The presence of the amino group is very important to the function and it is known that some representatives of this substance class lose this amino group when irradiated with UV. The reaction is formulated as an intramolecular hydrogen transfer from the amino group to the carbonyl oxygen and is analogous with the gamma hydrogen abstraction of aliphatic ketones (Figure 2.4.5).

To establish the reaction prerequisites, compounds 14-20 differing in the substituent in position 4 were prepared to evaluate the possibility of formation of deamination products. All compounds with an N-N bond in position 4 deaminated, while those with an N-C bond in this position did not (see Figure 2.4.6). The reaction is therefore independent of the presence of H atoms on the amino group. On the basis of these results, a Type II Norrish intramolecular formation mechanism must be abandoned. Such a mechanism would predict that compounds 19 and, especially 14, because of the possible formation of the 6-membered ring transition state, should react in the desired manner but that compounds 16 and 18 should not.

To clarify the effectiveness of this photochemical deamination the quantum

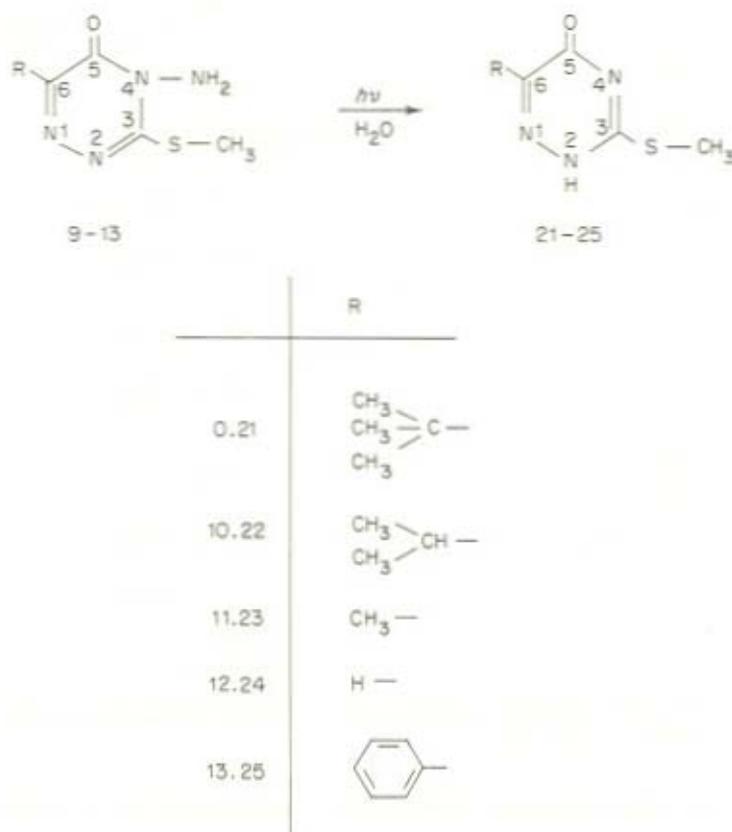


Figure 2.4.5 Photoreaction of 4-amino-3-methylthio-1,2,4-triazine-5(4H)-ones (9-13)

yields of the homologous series 9-13 were measured. Concentrations were determined by differential optical density measurements. This technique gives reliable results for small conversions provided the reaction proceeds uniformly, i.e. if the photo-products 21-25 alone are formed. Table 2.4.5 lists the values obtained in solvents saturated with air.

In terms of the observed quantum yields, the table shows that:

- the effects of water and oxygen on the deamination are clearly evident and that their combined action is required to produce a cleavage of the amino group,
- the proton in the deamino compound is derived from the solvent, thus, an intramolecular reaction is involved.

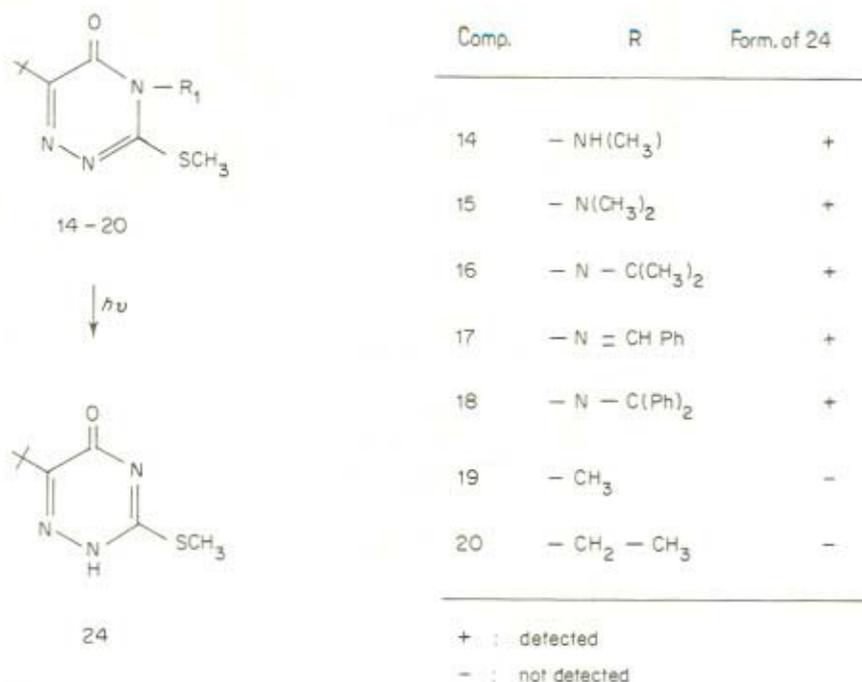


Figure 2.4.6 Photo-induced deamination reactions of some 3-methylthio 1,2,6-triazine-5(4H)-ones (14-20)

Table 2.4.5 Quantum yields of the photochemical deamination of the compounds 9-13

Compound	<i>p</i>		
	H ₂ O	H ₂ O/Dioxan (3:2)	Dioxan
9 21	8.16×10^{-3}	6.32×10^{-3}	1.0×10^{-4}
10 22	1.28×10^{-2}	0.90×10^{-2}	1.0×10^{-4}
11 23	1.16×10^{-2}	0.85×10^{-2}	1.0×10^{-4}
12 24	4.31×10^{-1}	3.65×10^{-1}	1.0×10^{-4}
13 25	2.90×10^{-1}	1.05×10^{-1}	—

Dechlorination of some chlorinated hydrocarbons

A third quantum yield example is the dechlorination of some aromatic chlorinated hydrocarbons. The UV spectra of the substituted benzenes shows all three bands (¹B_u, ¹L_a and ¹L_b) of the benzenes, although the high degree of symmetry of the aromatic compound is modified sharply by the substituents. Substituted benzenes experience a shift to longer wavelengths relative to

Table 2.4.6 Quantum yields of the photo-induced dechlorination of monosubstituted chlorobenzenes (26–34)

Compound	Dechloro product	1L_b	ρ
<i>o</i> -Dichlorobenzene (26)	Chlorobenzene (35)	271	2.44×10^{-1}
<i>m</i> -Dichlorobenzene (27)	Chlorobenzene (35)	273	4.17×10^{-2}
<i>p</i> -Dichlorobenzene (28)	Chlorobenzene (35)	274	4.48×10^{-3}
<i>o</i> -Chloroaniline (29)	Aniline (36)	292	6.20×10^{-5}
<i>m</i> -Chloroaniline (30)	Aniline (36)	292	4.29×10^{-2}
<i>p</i> -Chloroaniline (31)	Aniline (36)	300	—
<i>o</i> -Chlorophenol (32)	Phenol (37)	275	2.74×10^{-2}
<i>m</i> -Chlorophenol (33)	Phenol (37)	275	2.01×10^{-1}
<i>p</i> -Chlorophenol (34)	Phenol (37)	282	2.88×10^{-1}

benzene. The substitution also has an additional important effect. In benzene the transitions $^1L_a \rightarrow ^1A$ and $^1L_b \rightarrow ^1A$ are prohibited for reasons of symmetry, however, these transitions can occur in substituted benzenes. Thus, the values for the 1L_b bands, which are correlated with the dechlorination of the monosubstituted chlorobenzenes (26–34), increase from 140 in benzene to 352 in *o*-dichlorobenzene (26), to 3400 in *o*-chloroaniline (29) and to 5044 in *o*-chlorophenol (32). For the above reasons, these substances can also be dehalogenated in the layers of the atmosphere close to the ground where wavelengths greater than 290 nm are encountered. The dechlorination product formation quantum yields obtained with irradiation at the absorption maxima in *n*-hexane, differ from one another by powers of ten (Table 2.4.6). Chloroanilines (29–31), in which the *p*-chloroproduct is not dechlorinated, show a particularly great variation in yield. The quantum yield results also match three of the experiments carried out on the preparative scale.

As demonstrated by the examples presented in this paper, the quantum yield technique makes possible correlations between photochemical environmental stability and structural features of the organic compounds. The observed quantum yields, in fact, represent the only way to carry out reliable comparative photochemical studies based on the photochemical reactivity of carbon complex organic compounds.

2.4.3 DETERMINATION OF ENVIRONMENTAL PHOTOCHEMICAL DEGRADABILITY OF ORGANIC COMPOUNDS IN SOLID AND ADSORBED PHASE

Suspended matter is among the most important contributions to atmospheric contamination. Suspended particulates are always present in the air. Their chemical composition is complex and particle size varies. In polluted areas,

concentrations of suspended particles range from 60 to 200 $\mu\text{g}/\text{m}^3$ but peak values of 2000 $\mu\text{g}/\text{m}^3$ are not uncommon. Particle size is particularly important because it affects both the physical and chemical properties of the suspended matter. Particulates are influenced by the presence of different organic substances which constantly alter their chemical composition. As a consequence, it is difficult to treat these aerosols as scientifically definable entities. To characterize the state of environmental chemicals on surfaces, the relationship between the adsorption of these substances, pressure and temperature must be determined. It is also necessary to evaluate whether Freundlich isotherms adequately describe the distribution pattern and to consider whether heterogeneous surface effects, frequently encountered in nature, affect adsorption. There are examples comparing the adsorption behaviour of freons on Aerosil 200, silica gel and Sahara sand as a function of pressure and temperature. These show that the chemical composition of the adsorbent has little effect on the adsorption occupation density of the surfaces. Adsorption isotherms measured for silica gel corresponded to average isotherms of natural dusts. Therefore, at a maximum occupation density of 10^{15} particles per square centimetre, the adsorption can be described by Freundlich isotherms. The bond strength of 25 kcal/mol approximates other physical adsorption values and excludes the possibility of a special interaction with the surface giving rise to potential loosening of intramolecular interactions (Roth, Hoechst AG, 1978). However, the absence of energetic heterogeneity of the surface does suggest that a small proportion of the molecules are bound appreciably more firmly. Similar reasoning would explain why the heterogeneous composition of dust particles makes them susceptible to different atmospheric reactions, for example, the elementary photochemical smog processes.

Photo-induced reactions in the heterogeneous phase proceed differently from those in the homogeneous phase. Bond lengths and particularly bond angles between individual atoms are altered, therefore changes, generally of a bathochromic nature in absorption behaviour of the compounds, are much more important. The relative intensities of the individual bands also increase. As a consequence, those compounds whose homogeneous-phase absorption behaviour exclude absorption of light in the troposphere ($\lambda = 290\text{nm}$) are none the less excited in the heterogeneous phase. Chemical changes can then take place if these compounds have the right structural requisites. Furthermore, substances on surfaces are in a quasi-reactive state and the contact between these substances and atmospheric oxygen is magnified appreciably.

Bonds are broken and new bonds formed during a chemical reaction. The catalytic effectiveness of a surface is measured by its ability to accelerate electron transitions, therefore a knowledge of the distribution of the electrons in respective surfaces is important. It is the interaction between catalyst and

the substrate, attributable primarily to electron density and electron distribution, which governs the activity of the surface. Under favourable conditions, irradiation of a surface with visible or UV light can lead to a change in the distribution of the charge carriers of all the quantum states in the catalytically active surface. The result is a re-orientation of the excited bonds between the surfaces and the substrate atoms. To enable the photocatalytic reactions of organic chemicals to proceed, the surface must fulfil certain requisites. It must have a large number of active centres and if possible these should be identical because the catalytic step proceeds via identical bonds between substrate and surface.

The literature documents the use of certain semi-conductor oxides to obtain a dramatic increase in product yield during dehydrogenation of organic hydrocarbons by UV light (Wenneberg, 1967). Another important catalytic reaction is the oxidation of carbon monoxide in the presence of zinc oxide (Schwab *et al.*, 1964). Paraffins and olefins are also known to react to form peroxides, even at room temperature, if titanium dioxide is present. This type of catalytic behaviour indicates that it is perfectly feasible to predict that such reactions take place in the environment on natural surfaces such as sand and stone. A prime requirement for evaluating the contribution of photocatalysis to the transformation of environmental chemicals is thus the determination of the absorption behaviour of the test substance on natural surfaces.

2.4.3.1 UV behaviour of environmental chemicals in the heterogeneous phase

Reflection measurements make it possible to determine the UV behaviour of the relevant environmental chemicals in the adsorbed form. Specific bands responsible for the photo-induced transformation may be displaced bathochromically under these circumstances and their intensities may be changed if their absorption is extended to beyond 290 nm in the adsorbed phase.

The absorption behaviour of organic chemicals on surfaces cannot be described by the Lambert-Beer law because it does not account for diffuse reflection. Diffuse-reflection can be represented mathematically as follows (Kubelka and Munk, 1948):

$$F(R_{00}) = \frac{(1 - R_{00})}{2R_{00}} K$$

Here R_{00} is the relative diffuse reflectance of an infinitely thick layer referring to a non-absorbing standard such as silica gel, magnesium oxide, etc. K is defined as the absorption coefficient of the relevant substance. The so-called diffuse reflectance can be estimated from theoretical considerations. However, the value obtained represents the total reflection made up of a

diffuse and a specular component. Specular or regular reflection is the mirror-type reflection of the plane surfaces of powdered crystals. By contrast, diffuse reflection occurs when the radiation penetrates into the interior of the powder, passes through one or more crystals and regains the surface only after suffering multiple scattering within the layer. The specular reflection is given by the following equation:

$$R_{\text{ref}} = \frac{I_{\text{ref}}}{I_{\text{s}}} \frac{(n-1)^2 + n^2x^2}{(n+1)^2 + n^2x^2}$$

where n is the refractive index and x is proportional to the absorption coefficient. For substantial values of x , i.e., strong absorption:

$$n^2 + 1 + n^2x^2 = 2n$$

In the case of strong absorption therefore, $R_{\text{ref}} = T$. This means that the crystal displays a high specular reflectance within the region of its strong absorption bands. When the crystal is comminuted. The proportion of the specular reflection falls, but is not entirely eliminated. The effect of the specular portion on total reflection is revealed in Figure 2.4.7.

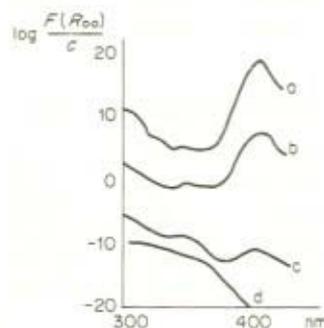


Figure 2.4.7 UV-spectra of anthracene adsorbed on silica gel. a = 0.001 per cent anthracene, b = 0.01 per cent anthracene, c = 0.1 per cent anthracene, d = pure anthracene.

To match theoretical considerations the spectra should be recorded in strong dilution. A measurement of pure anthracene, against silica gel as standard, does not show the intense band at 410 nm. However, if the samples are diluted with silica gel, this absorption band becomes progressively more evident (Kortüm and Schreyer, 1956). Monosubstituted chlorobenzenes also display shifts and increases in intensity. A comparison of the absorption spectra of some representatives of this substance class, both adsorbed on silica gel and in solution with hexane, demonstrates the effect of surface adsorption on the UV behaviour of these substances (see Figure 2.4.8).

An increase in intensity and a bathochromic shift are particularly evident

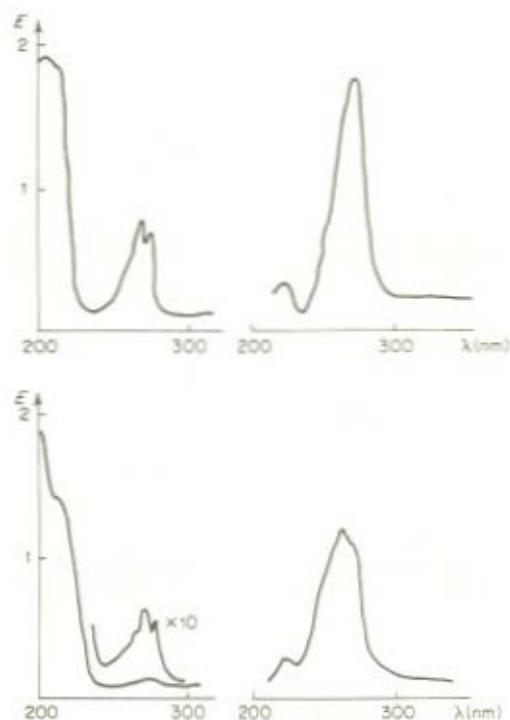


Figure 2.4.8 UV-spectra of *o*-chlorophenol and *o*-dichlorobenzene in solution and adsorbed on silica gel

in the 1L_b bands. These changes may well be responsible for the dechlorination of these substances. The displacement means that these bands enter the spectral region of available light energy in the troposphere. The UV spectra of some chlorinated hydrocarbons, often regarded as model environmental chemicals, confirm how much the absorption changes depend on the state of the molecule (Figure 2.4.9). Bathochromic shifts of between 0 and 40 nm and up to 50-fold increases in intensity are observed. Photodieldrin, for example, displays a very marked bathochromic displacement combined with a strong widening of the absorption band (Figure 2.4.10). The absorption peak for photodieldrin, which occurs at 193 nm in hexane, is displaced by 71 nm to 264 nm when the compound is in an adsorbed state.

These examples make it clear that even substances without a chromophoric group can be activated in the adsorbed state. The result of such an activation is a possible transformation or degradation of the compound under the photochemical conditions of the lower atmospheric layers.

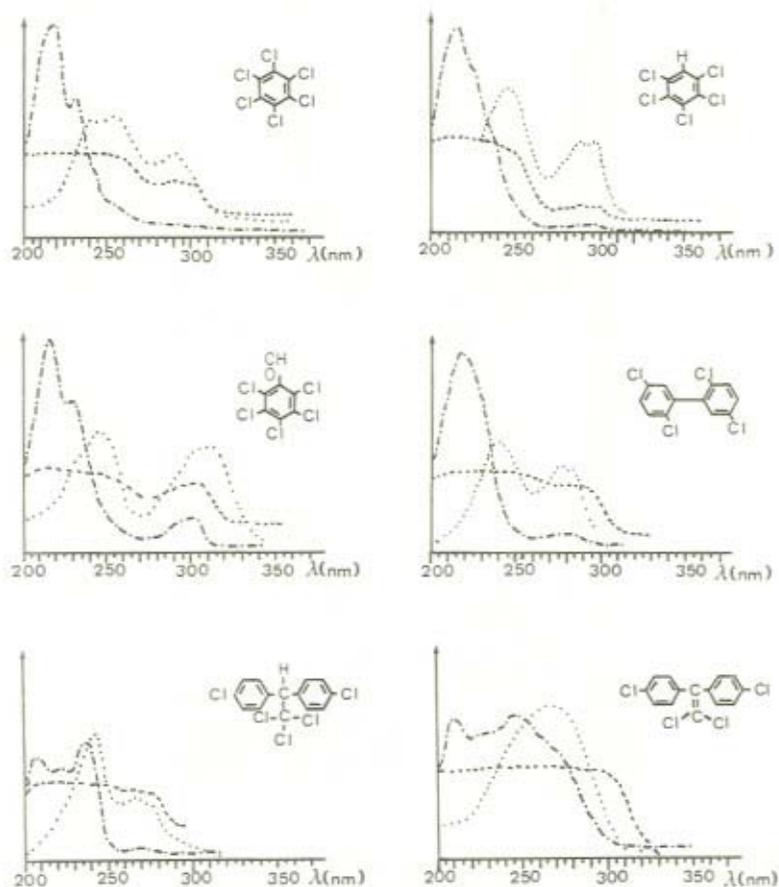


Figure 2.4.9 UV-spectra of some chlorinated hydrocarbons. --- = in *n*-hexane, — = as solid, ··· = adsorbed on silica gel

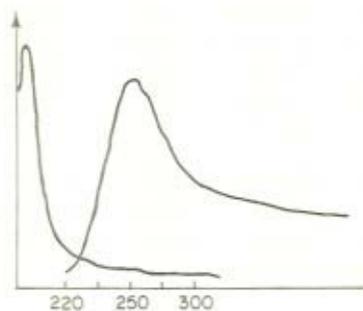


Figure 2.4.10 Absorption spectra of photo-dieldrin (λ_{\max} in *n*-hexane = 193 nm; λ_{\max} adsorbed on silica gel = 264 nm)

2.4.3.2 Phototransformation of organic chemicals to inorganic products (photomineralization)

The initial photomineralization research was concerned primarily with reactions of chlorinated hydrocarbons both as solids and adsorbed on standardized surfaces. These experiments revealed that many chlorinated hydrocarbons, which normally rank as the most stable environmental chemicals, were degraded to carbon dioxide by irradiation with light of wavelengths greater than 290 nm (Table 2.4.7). Studies of DDT, DDE and pentachlorophenol indicated that the photo-oxidative degradation of substances adsorbed on silica proceeded considerably faster than degradation of the solid form (Gäb *et al.*, 1974).

The available experimental data does not confirm that the cause of mineralization is the superior distribution of the substance on an adsorbent of large specific surface area thereby making it more accessible to a photo-induced oxidation. Nor do the results show whether catalytic effects are important in determining the course of the reaction. It is clear, though, that many photo-chemical reactions are blocked under these conditions. Oxidations ensue more rapidly, while isomerization and dehydrohalogenations are suppressed. Such behaviour is understandable as it is well known that the above reactions proceed via a triplet state which excess oxygen blocks entirely. The compounds isolated and examined from these experiments provide no concrete information about the active oxygen species. It is assumed that O^3P atoms may be the agents responsible, as they are in fast phase experiments carried out with the same model substances.

Table 2.4.7 Photo-induced decomposition of the solid form of some chlorinated hydrocarbons to CO_2 and HCl

Compound (80 mg)	Quartz filter (2 days)		Pyrex filter (6 days)	
	CO_2	HCl	CO_2	HCl
	in mg		in mg	
Aldrin				
Dieldrin	51-70	19-28	8-11	3-4
Photodieldrin				
Hexachlorobenzene				
Pentachlorobenzene	46-53	19-26	—	—
2,2',4,4',5,5'- Hexachlorobiphenyl				
Pentachlorophenol				
DDT			10-15	2-8
DDE				

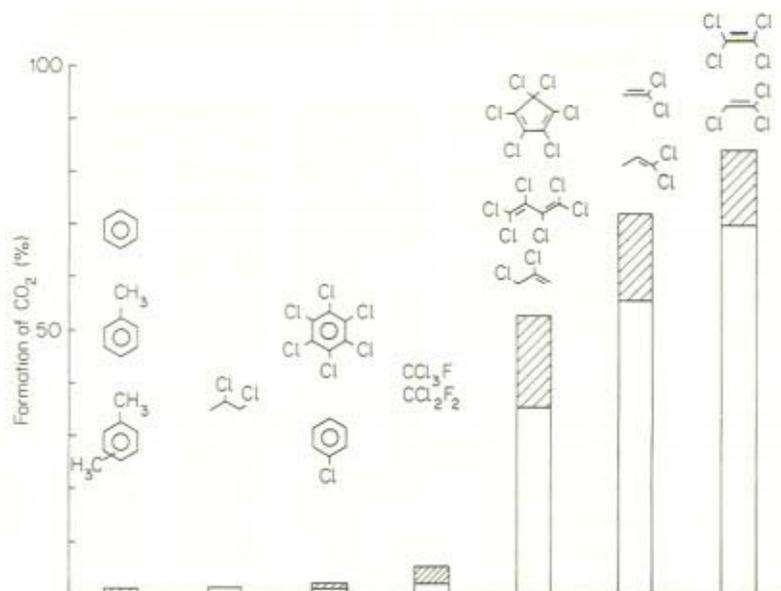


Figure 2.4.11 Photomineralization of some chlorinated olefins, fluorocarbons, chlorinated alkanes and aromatic compounds

Another important result of these studies is that chlorinated olefins are converted more rapidly under quartz irradiation conditions. Simple aromatics such as benzene, toluene and *ortho*-, *meta*- and *para*-xylene also behaved similarly. After six days the yield of mineralization products was less than 1%, with the xylenes being broken down more rapidly. Other aromatic compounds with side-chains were found to behave in a like manner (see Figure 2.4.11) (Gäb and Korte, 1978).

TCDD (2,3,7,8-Tetrachlorodibenzo-*p*-dioxin) can also be broken down completely when adsorbed on silica gel by irradiation of wavelengths greater than 290 nm.

From the available data it is postulated that mineralization represents a chlorine-induced photo-oxidation (at least in the case of the chlorinated hydrocarbons). In the first step of the reaction the C-Cl bonds are cleaved, and these products then continue to attack the organic compounds in the ways analogous with the mechanism underlying auto-oxidations.

2.4.3.3 Photomineralization of freons

A very important current problem in atmospheric chemistry is whether the troposphere can provide a sink for fluorocarbons, which are among the most stable chemicals in the environment. Investigations carried out with ^{14}C -labelled substances on various natural surfaces have shown clearly that

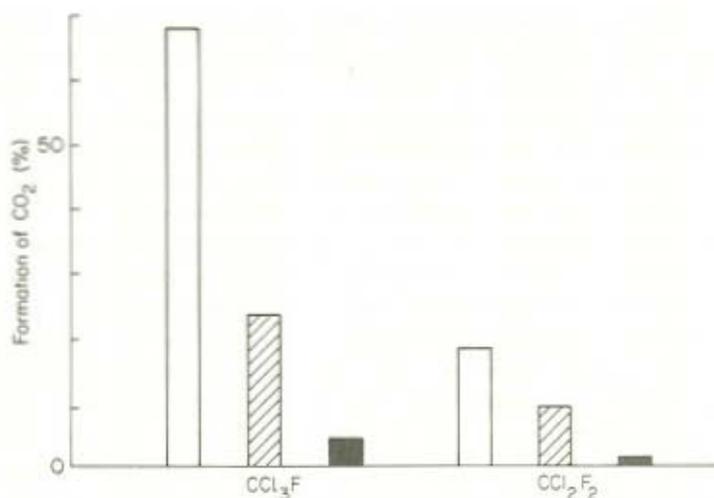


Figure 2.4.12 Rates of degradation of CCl_2F_2 and CCl_3F . The percentages given are the ratio of carbon dioxide formed to that theoretically possible. A mercury high-pressure lamp (HPK 125 W, Philips) was used for the irradiation. \square = 48 h through quartz glass ($\lambda > 230$ nm), ▨ = 144 h through Pyrex glass ($\lambda > 300$ nm), \blacksquare = Irradiation with sunlight close to the ground for effectively 170 h (7–28 September 1977)

these substances can be broken down to carbon dioxide under the action of sunlight.

Figure 2.4.12 shows the degradation rates of CCl_2F_2 and CCl_3F in terms of carbon dioxide formed (Gäb and Korte, 1978). The percentages given are the ratios of measured to theoretically possible carbon dioxide. By comparison, irradiation with wavelengths shorter than 290 nm produced a markedly higher degree of breakdown after only two days than irradiation with wavelengths greater than 290 nm for six days. Homogeneous photolysis is a mechanism which provides a probable explanation of this phenomena. Irradiation under outdoor conditions also produces higher rates of breakdown than irradiation through borosilicate glass. If the amount of chlorine and chloride formed rather than the carbon dioxide produced is chosen as the criterion for assessing mineralization, a different picture is obtained. However, a comparable decrease is evident when Pyrex-filtered UV light and sunlight are used rather than short-wave UV light. Another feature of the mineralization process is the production of CO as well as CO_2 , while chlorine is formed only during irradiation through quartz. It is not as yet clear whether a decomposition induced by chlorine radicals takes place as well. Irradiating carbon tetrachloride, trichlorofluoromethane and dichlorodifluoromethane adsorbed on sand in the presence of ethane,

Ausloos (1977) demonstrated the formation of chlorine-containing products, for instance chloroethane. Rasmussen (1978) found evidence of a measurable photolysis of fluorocarbons above and in the air. It is clear that transformation of stable compounds on surfaces is an important sink in nature. However, the rate at which the reactions occur in the troposphere cannot be precisely estimated at present. Due to energetic differences of surfaces, errors may be introduced into determinations of tropospheric residence times. Absorption energy diminishes as fluorocarbon partial pressure decreases, and it is therefore premature at present, to attempt to correlate the rate of degradation with tropospheric conditions using data obtained at a partial pressure 10^8 times greater than in the troposphere.

It can be stated, however, that the rate of photomineralization of fluorochlorocarbons is slower than that of chlorinated olefins by a factor of 10–20 but comparable to that of some methyl and chlorine substituted benzenes. It is also recognized, moreover, that mineralization of fluorocarbons can be initiated by surface catalysis. Results suggest that drying of natural surfaces, for instance Mecca sand, activates the available surface sites for catalysis. These active centres become blocked after the reaction has taken place and are not available for further reactions. However, some allowance must be made for the availability of those surface sites responsible for the strong adsorption of these compounds and their subsequent unavailability for catalysis. Investigations carried out on silica gels suggest that the energetic heterogeneity of the surfaces causes a small proportion of the molecules to be bound appreciably more firmly, thus enabling oxidative breakdown to occur. Such reactions probably do occur in nature, for example in steppe and desert regions, and they may represent a sink for fluorocarbons.

2.4.3.4 Efficiency of photomineralization experiments

If different substance classes are investigated under standardized conditions, it would appear possible to obtain correlations between structural features of these organic chemicals and their degradation. There are two basic experimental routes:

- (a) A study of the behaviour of the environmental chemicals under natural or simulated conditions;
- (b) A study of the individual reaction steps with the aid of steady-state kinetics.

Naturally, the realization of natural boundary conditions presents great difficulties. Solid and liquid aerosols, and also soil and water surfaces, are difficult to manipulate. Furthermore, for such experiments, concentration ranges of the test compounds should be selected to approximately correspond to natural environmental levels. Because of limitations imposed by the

analytical methods, for example the limits of detection of individual compounds, this ideal is not always possible. Environmental chemicals behave very differently when in extremely dilute concentrations, it is therefore often necessary to work with radioactive labelled substances. Such experiments enable a balance between realistic concentrations and detectability to be maintained. Isolation and identification of intermediate products is also facilitated.

Individual kinetic studies are much easier to manage experimentally than are natural or simulated environmental experiments. For kinetic studies, laws governing the photochemical degradation of adsorbed-phase organic chemicals can be developed using the techniques of quantum yield, optical extinction diagrams and the other methods previously discussed. Should such a procedure prove to be possible, then compounds of a particular substance class could be classified in respect of their photochemical degradability when adsorbed on surfaces. Both gas chromatographic and UV reflection measurements can be used to determine quantum yield. In some instances total absorption can be attained. In such cases, it is useful to determine both the absorbed and the reflected light. Where a pure compound is tested, the decrease in starting compound and the product formed can be measured solely by UV spectroscopic means. Differential extinction techniques are employed for measuring the compound degradation. Since the primary photochemical transformation depends on the absorption of the relevant substance on surfaces, different concentrations would have to be used to determine relative degradability of the model substances. An attempt should also be made to evaluate correlations between other physical parameters and the rate of photomineralization.

To date, the rates of photo-oxidations, isomerizations and dehalogenations can be correlated with the ionization potentials of test compounds. Table 2.4.8 lists the ionization potentials and the relative photomineralization rate

Table 2.4.8 Photomineralization rates and ionization potentials of some organic molecules

Compound	Photomineralization (%CO ₂)	Ionization potential (eV)
Aniline	46.5	7.70
Naphthalene	30.0	8.12
Benzene	15.2	9.24
Benzoic acid	10.2	9.73
Nitrobenzene	6.7	9.92
Acetic acid	6.6	10.36
Carbon tetrachloride	1.0	11.47

of selected chemicals. The data show that a satisfactory correlation exists between the photomineralization of these chemicals and their ionization potentials (Parlar *et al.*, 1982).

This correlation suggests the possibility of estimating the photochemical degradability of environmental chemicals merely from the measurements of their ionization potentials. It seems likely that such a correlation would be subject to some error. However, satisfactory results from a series of photodechlorinations (which proceed by photochemical induction) and also from photomineralization experiments carried out with ^{14}C -labelled compounds, suggest that photo-electron spectroscopy is a suitable technique for making comparative assessments.

2.4.4 CONCLUSIONS

Irradiation experiments in solutions have clearly shown that photo-isomerization and photo-dechlorination reactions can readily occur under natural conditions, if the substance fulfils structural requisites. Studies of contaminants using kinetic measurements comprise a simple set of methods for determination of the photostability of organic chemicals in liquid phase. In order to estimate the behaviour of organic substances in natural waters, kinetic experiments with reactive oxygen species are desirable. With experiments designed to produce quantum yield data, it is possible to compare the photostability of chemicals and to develop structure-degradability relationships.

The results presented in this work also point unambiguously to the possible existence of a tropospheric sink for environmental chemicals. Natural surfaces such as sands, minerals and aerosols are superabundantly available, and active surface centres are constantly being re-formed by natural processes. For instance, the formation of desert aerosols is estimated to proceed at the rate of 2000 million tons annually. It is logical to postulate that photo-induced degradation of surface-adsorbed chemicals is one of the principal transformation processes of industrial chemicals. The quantitative importance of these heterogeneous processes needs to be verified by way of more sophisticated simulation experiments.

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