ECOTOXICOLOGY AND ENVIRONMENTAL SAFETY 2, 219–232 (1978)

Organochlorine Compounds and their Reactions in the Atmosphere[1]

HARUN PARLAR

Institut für Ökologische Chemie der Gesellschaft für Strahlen- und Umweltforschung mbH München, D-8051 Attaching, and Institut für Chemie der Technischen Universität München, D-8050 Freising-Weihenstephan, FRG

Received June 1, 1978

To estimate the influence of the chlorinated hydrocarbons on the quality of the environment, primarily chemico-ecological and toxico-ecological data are required. In addition to their level of production, range of application, and distribution tendency, a knowledge of their transformation under environmental conditions is desirable. On one hand, the change of a substance under biotic and abiotic environmental conditions provides an indication of whether an enrichment of the environment with the relevant chemical may be anticipated in the long term; on the other hand, these investigations allow possible persistent transformation products to be characterized. In contrast to the biological degradation pathways and transformation processes of environmental chemicals, whose course is accompanied by only very small amounts of energy, energy sources with an inexhaustible capacity and constant intensity are available for abiotic conversions. Temperature and uv radiation become the most important manifestations of the largest energy source of our environment, the sun, whose direct or indirect effect is especially important during an ecological assessment of chlorinated hydrocarbons. It is also important to know in which ecological systems these chemicals occur, because both dynamic and catalytic effects can be traced back primarily to the respective state of the molecule and the interaction with the surroundings. In this connection the task posed is an investigation of the reactions of chlorinated hydrocarbons under simulated atmospheric conditions. Such simulations are made more difficult by virtue of the complexity of these reactions. The atmosphere may be portrayed as a large chemical reactor in which complicated reactions take place under the action of the sun's uv radiation and are catalyzed by trace substances and whereby large amounts of substances are reacted. Numerous equilibria are established under the influence of chemical, photochemical, and physical factors. To study individual reaction mechanisms, it is necessary to create conditions which correspond to those in the atmosphere, or a partial simulation to enable the experimental results to be interpreted with some degree of probability

A study of the reaction of the chlorinated hydrocarbons in the troposphere presupposes a knowledge of the physical parameters of the troposphere. A look at the temperature profile of the troposphere reveals temperatures between 200 and 300°K depending on geographical location and height. The radiation intensity of the sun, too, is primarily regulated by height. Figure 1 shows the solar radiation intensity as a function of wavelength (Hines, 1965). Only 5–6% of the total radiation intensity is contributed by the uv portion between 290 and 400 nm that is responsible for many reactions taking place in the troposphere, but it amounts to nearly 10% of the total solar energy in the

[1] Presented at the 5th International Symposium "Chemical and Toxicological Aspects of Environmental Quality," Munich, September 21 and 22, 1977.

0147-6513/78/0022-0219$02.00/0

troposphere. Wavelengths below 290 nm are absent from the troposphere because of absorption in the ozone layer. As is shown by the figure, the intensity maxima of the solar radiation are at 440–460 nm.

If we consider an organochlorine compound located in the troposphere independently of whether this substance is present in the gas phase, as a solid, or in the dissolved form, and if we assume that it cannot absorb uv light above 290 nm, then in theory only one type of reaction is possible for this compound. The reactive species in the troposphere (among them NO_2, O_3, $^3O_2$) can attack the molecule. Thus, if the organohalogen

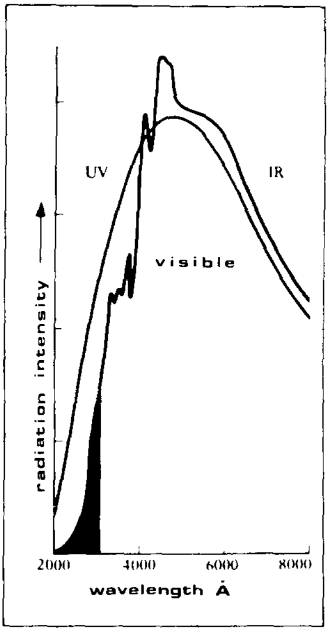


FIG. 1. Solar radiation intensity as a function of wavelength.

compound fulfills the structural requisites it could undergo reactions with these species leading, possibly, to intermolecular products. On the other hand, if the basic skeleton or the functional groups of the molecule or the combination of the two make uv absorption possible, then the following photophysical and photochemical component steps may be anticipated (Scharf and Fleischhauer, 1975) (Fig. 2): (a) dipole transitions; (b) radiation-free transfer; and (c) energy transfer which, in turn, may be divided into two groups: (1) energy transfer by radiation and (2) radiation-free energy transfer.

(*a*) *Dipole Transitions*

On absorbing a photon, a molecule with complete electron shells is excited from a singlet ground state (S_{00}) into the vibration level of a higher electron state S_{nl} of equal multiplicity (Process 1) in accordance with the selection rules. Transitions into an excited triplet state (Process 2) are also possible but are seldom observed because of the small transition momentum. Return reactions of Processes 3 and 4 are termed phosphorescence and fluorescence. Fluorescence could also arise, for example, from the first triplet state, T_{10}, with the radiation-free transitions leading to the first singlet state. Normal fluorescence then follows. This Process 5 is known as delayed fluorescence.

(b) Radiation-free Transfer

From the S_{1L} state (excited singlet state) the molecule rapidly passes into the S_{00} state without radiation. Such a radiation-free transition between equal multiplicities is known

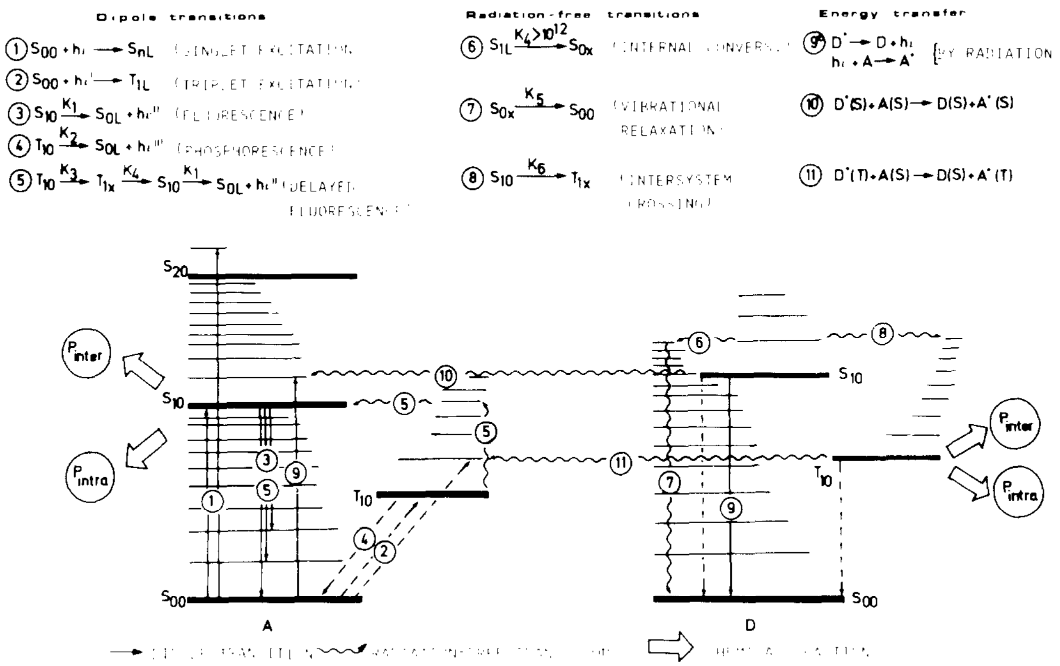


FIG. 2. Possible photophysical and photochemical processes of molecules.

as internal conversion. Two steps mark the actual process; namely, the actual "internal conversion," i.e., the transition from the excited singlet state (S_{1L}) into a degenerate or quasidegenerate state (S_{0L}) (Process 6), and the following transition from S_{0L} to S_{00}. This second step is referred to as vibrational relaxation (Process 7). The internal conversion, which can also take place between the excited triplet states, is a consequence of the overlapping of the potential hypersurfaces of the two excited states. A further noteworthy fact is that the rate constant of Reaction 6 is $K_4 = 10^{12}\ \mathrm{sec}^{-1}$. In contrast, Process 7 proceeds only very slowly because of the small energetic difference. It is the internal conversion which explains why, especially in the condensed phase, chemical reactions occur preferentially from the first singlet or triplet level (Kasha's Golden Rule). It is perhaps important also to emphasize that the deactivation processes in the condensed phase are of a biomolecular nature and for this reason proceed in a diffusion-controlled manner. For the further photochemical reactions the activation energy is very small, because the molecule obtains an adequate excess of energy by absorption of a photon. Each collision of the partners brings about a reaction, and the reaction velocity is governed solely by the diffusion rate of the reaction partners; i.e., it is dependent on the temperature, viscosity, and lifetime of the excited species.

During internal conversion, the radiation-free process takes place between states of equal multiplicity. If this conversion occurs between states of different multiplicity (Process 8), it is referred to as intersystem crossing or spin-system changing. Except for the spin reversal this process is identical in its mechanism with internal conversion. The component layer of Process 5 during delayed fluorescence is also an intersystem crossing.

(*c*) *Energy Transfer*

The energy transfer, which plays a particularly important part in photochemical processes, may be divided into two groups:

(*1*) *Energy transfer by radiation.* In Process 9, an excited donor molecule returns to the ground state and the quantum that is formed can excite an acceptor molecule. There is no need for an interaction between acceptor and donor molecules; it is only necessary that the emission spectrum of the donor molecule and the absorption spectrum of the acceptor molecule have overlapping regions as wide as possible. This transfer of energy ensues radiatively because a photon always participates.

(*2*) *Radiation-free energy.* This can emanate either from a singlet-excited donor molecule (Process 10) which excites an acceptor molecule in a singlet mode, or from a triplet-excited donor molecule which transfers its energy once again to an acceptor molecule also in the triplet state. All the mechanisms itemized so far are transitions which in chemical terms lead to no change but are responsible for the individual component steps and reactions. They are simplified consideration which make very complicated reaction modes more comprehensible. However, from the viewpoint of environmental quality, it is primarily the chemical reaction that is important. The reaction can proceed from the singlet or also the triplet state of the molecule.

During chemical changes in organochlorine compounds in the troposphere the reaction pathways illustrated in Fig. 3 are possible. This figure illustrates the possible chemical reactions of chlorinated hydrocarbons in the troposphere schematically. Compound A absorbs a photon and is converted into an excited state. As has already

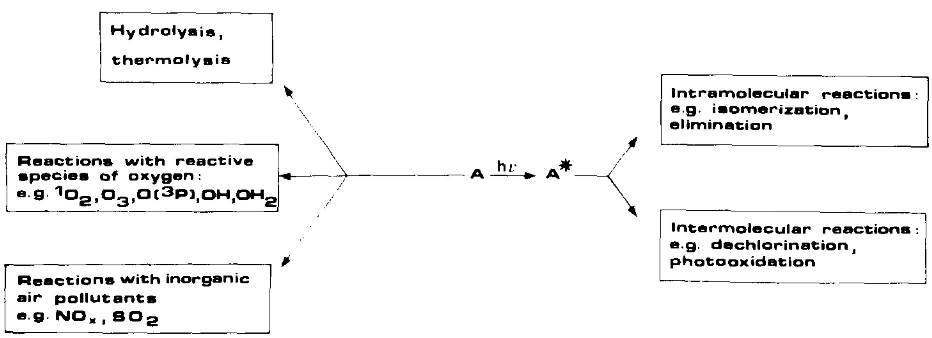


FIG. 3. Possible chemical reactions of chlorinated hydrocarbons in the troposphere.

been mentioned two reaction pathways are possible from here: (a) Intramolecular reactions whose course is controlled by the excited state; no partners are required for these reactions and for this reason they occur preferentially over the possible intermolecularly proceeding reactions; and (b) intermolecular reactions, for example, dechlorinations, which are reactions with different active or inactive species in the troposphere which can proceed in the presence of proton donors. Such reactants can accumulate either by virtue of urbanization, examples being NO_x or SO_2, or they can gather in the troposphere by virtue of transfer mechanisms involving energy resulting in the formation of oxygen. Singlet oxygen or oxygen atoms $O(^3P)$ are examples.

During the photomineralization reaction several oxygen species are very likely. These lead to the total oxidation of the molecule; i.e., the organohalogen compound is converted into CO_2, HCl, and Cl_2.

(*a*) *Intramolecular Reactions of the Organochlorine Compounds*

Two selected examples should demonstrate the importance of this type of reaction:

(*1*) *Photoisomerization reactions of chlordene isomers.* The compounds referred to in the literature as α- and γ-chlordene (**1** and **2**) are isomers of chlordene whose structures have been positively identified by means of spectroscopic data. Their proportion in technical chlordan, which ranks among the best known cyclodiene insecticides, amounts to about 21–24% including the β-isomers. Ultraviolet irradiation of these compounds leads to photoisomerization products formed by (2 + 2)-cycloaddition (**3** and **4**). The reaction is strictly intramolecular and furnishes the photoproducts in very good yields; the insecticidal effectiveness of these products were determined by means of tests on *Musca domestica* and *Spodoptera littoralis* (Gäb et al., 1975a). Figure 4

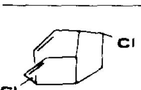
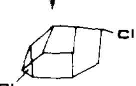
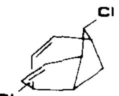
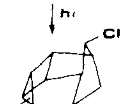
Compound	% Lethal 10 ug/Fly	LD_{50} ug/Fly	Toxicity index Parathion = 100	% Lethal 4 %	LC_{50}	Toxicity index Parathion
 Cl_5 (1)	45	---	---	0	--	---
↓ hν						
 Cl_5 (3)	100	0.41	13	80	0 25	8
 Cl_5 (2)	5	---	---	10	--	---
↓ hν						
 Cl_5 (4)	100	0 35	15	20	--	---
Parathion	100	0 052	100	100	0 031	100

FIG. 4. Photoisomerization reactions of chlordene isomers and their insecticides' effectiveness.

shows the results. By comparison with the familiar component of technical chlordan (heptachlor and the chlordan isomers) α- and γ-chlordene (**1** and **2**) display a lower insecticidal activity. In contrast, photoproducts **3** and **4** are more toxic to *Musca domestica* and *Spodoptera littoralis* than the starting compounds. For example, 10 g of α-chlordene (**1**) per fly kills only 45% of the animals used, while the same quantity of photoisomerization product (**3**) produces 100% lethality. In the case of γ-chlordene (**2**) the ratios are even more impressive. Photo-γ-chlordene (**4**) is almost 20 times as active

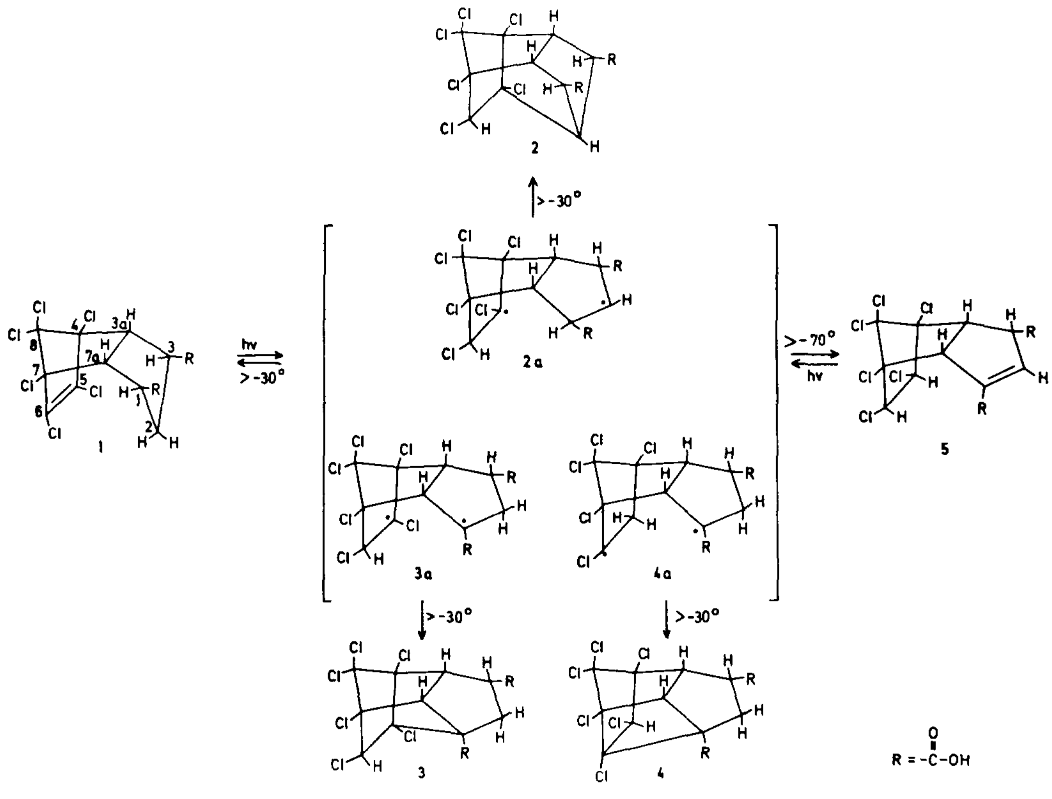


FIG. 5. Photoinduced hydrogen transfer reaction of aldrindicarboxylic acid (**1**).

as its parent compound (**2**). A comparison of the other data such as LD_{50} or LC_{50} with parathione shows the strongly enhanced insecticidal activity of the photoproducts. Particularly noteworthy is the lethality of photo-α-chlordene (**3**) in the *Spodoptera littoralis* test; here the use of 4% sprays of this compound killed 80% of the experimental animals used. A repeated test with parathion clearly shows the insecticidal activity of this compound.

(*2*) *Photoinduced hydrogen transfer reactions.* During the sensitized irradiation of the dihydrochlordene derivatives we also observed intramolecularly proceeding reversible and irreversible hydrogen shifts in addition of the ($\pi\sigma \rightarrow 2\sigma$)-reaction typical for this class of substances (Parlar *et al.*, 1975). This type of suprafacial displacement of two hydrogen atoms from saturated to unsaturated systems is termed a synchronous reaction among the group transfer series. In constrast, in a nonconcerted process it is possible in the first step of the reaction for radicals that have formed to stabilizeeither by recombination or by displacement of a second hydrogen atom with formation of a new double bond. Quite fundamentally the alkene–alkene pair formed in this way can also be used in the back-reaction to the corresponding starting compounds.

The uv irradiation of aldrin dicarboxylic acid (**1** in Fig. 5), which is a terminal metabolite of aldrin and dieldrin in biological systems, furnishes exclusively 4,5,6,7,8,8-hexachloro-8a,4,5,6,7,7a-hexahydro-4,7-methano-1,3-dicarboxylic acid (**5**), which at temperatures above $-30°C$ forms the starting compound **5** by photoisomerization. Isolation of compounds **2**, **3**, and **4** which, formally, may be described as C2 → C5 and C1 → C6 bridged products of **1** and **5**, points to the existence of biradical intermediate stages. The reversible intramolecularly proceeding photoreaction between **1** and **5** can be sensitized in solution with the familiar triplet sensitizers acetone and acetophenone. In contrast, the triplet energy transfer cannot be achieved by excited benzophenone with a triplet energy of 69.2 kcal/mol. It follows that the lowest-energy triplet states of **1** and **5** lie between 69.2 and 76.3 kcal/mol. The quantum yields of the formation of **1** and **5**, $\Phi = 1.98 \times 10^{-2}$ and $\Phi = 0.04 \times 10^{-2}$, suggest that the photoequilibrium is displaced in favor of **5**. It is evident from the results of this study how complicated the intramolecular process can be and how from one single compound four intramolecularly formed isomers of the starting compound have been formed here. These compounds must be accounted for in the chemico-ecological assessment of the aldrin–dieldrin insecticides and included in the toxicoecological investigations.

(*b*) *Intermolecular Photoreactions*

(*1*) *Photodechlorination reactions.* Approximately 40% of pesticides contain chlorine, which in many instances is coresponsible for the effectiveness and the toxicity of these substances. In many cases detoxication can be achieved by dechlorination of the chlorinated hydrocarbons. Either biological conversion or uv radiation in the atmosphere can bring this about. Two selected examples should make the structural circumstances of the starting compound during dechlorinations clear:

(*1a*) *Photodechlorination of monosubstituted chlorobenzenes.* First, these compounds are perfectly suitable as model substances for such investigations. Second, some of them are breakdown products of important pesticides that are used in large quantities: for instance, the chloroanilines, degradation products of phenylurea herbicides, and the chlorophenols, degradation products of carbamates; therefore the study of quantum yields is of ecological interest just on this count. With respect of the substituent and the position relative to chlorine, comparative studies can provide important information. If the distribution mechanism and the absorption bands of the substances are known, on aerosols as well, than the conversion rates can be calculated as a function of height and regional location. There is a strong mutual deviation within a group in the quantum yields of the dechlorination reaction. This deviation is on the order of one power of 10 among the *ortho*, *meta*, and *para* products of chlorobenzenes and chlorophenols and as much as 3 powers of 10 among those of chloroanilines (Steven, 1974) (Fig. 6). It was found during the investigation of phenylurea herbicides and higher chlorinated anilines

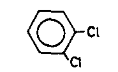
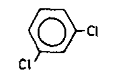
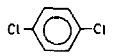
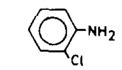
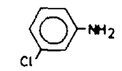
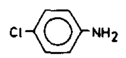
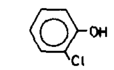
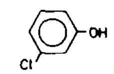
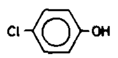
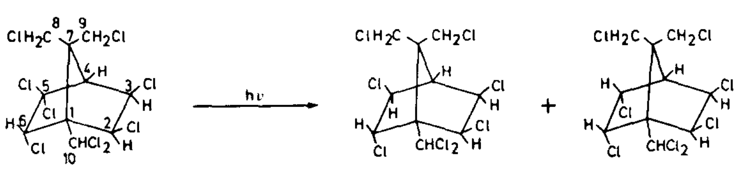
Compound	Φ	λ_{max} [nm] ^1L_b-band
	2.44×10^{-1}	271
	4.17×10^{-2}	273
	4.48×10^{-3}	276
	6.20×10^{-5}	292
	4.29×10^{-2}	292
	---	300
	2.74×10^{-2}	275
	2.01×10^{-1}	275
	2.88×10^{-3}	282

FIG. 6. Quantum yields of formation of the dechlorination product of dichlorobenzene, chloraniline, and chlorophenol in *n*-hexane.

and phenols that chlorine in the *meta* and *ortho* positions is degraded faster than when it is in the *para* position. The results obtained point to the fact that the substituent and its position are two features that should be paid more attention during selection of pesticides. There is thus the possibility of producing effective but at the same time environmentally conservative preparations.

(*1b*) *Ultraviolet dechlorination behavior of the insecticide toxaphene.* Toxaphene is a mixture of higher chlorinated C_{10} hydrocarbons of predominantly bornane skeleton



I Ia Ib

FIG. 7. Photodechlorination of "Compound I" at wavelengths above 230 nm.

structure. The results of several groups have shown that during preparation of this compound a Wagner–Meerwein rearrangement takes place (Parlar *et al.*, 1977); the mixture is prepared by chlorinating camphene. Approximately 180 different chlorinated hydrocarbons are contained in the mixture. The photochemical behavior of "Compound I" (Anagnastopoulos *et al.*, 1974) was investigated (Parlar *et al.*, 1976). In addition to a dehydrohalogenation product, two dechlorination products (Ia and Ib) were identified (Fig. 7). Dechlorination takes place on the C_5 atom; neither the $-CHCl_2$ group on C_1 nor the CH_2-Cl group on C_7 are attacked. Further dechlorination does not take place. From this experiment the following conclusions can be derived: (a) Chlorinated bornane derivatives are dechlorinated only if they have a $-CCl_2$ group on the ring; (b) the side-chain $-CHCl_2$ group was not attacked; and (c) dehydrohalogenation takes place only if the compound has a $-CCl_2$ group in the ring. It is evident from this result that the structure and more especially the position of the chlorine atoms control the dechlorination in such way that selective dechlorinations are perfectly feasible.

(2) *Reactions of chlorinated hydrocarbons with reactive oxidizing agents.* During transformation of chemicals under atmospheric conditions the reactions with different oxidizing agents in the troposphere play an important role. In the ground state the oxygen molecule possesses two unpaired electrons; i.e., a triplet state ($^3O_2$) obtains and is paramagnetic. The Franck–Condon diagrams for various states of the oxygen molecule are given in Fig. 8. From the forbidden transitions of the ground-state oxygen ($^3\Sigma g^-$) two different singlet oxygen molecules are produced, namely, $^1\Delta g$ and $^1\Sigma g^+$. The transition $^3\Sigma g^-$ to $^1\Delta g$ occurs in the "infrated atmospheric system," the transition $^3\Sigma g^-$ to $^1\Delta g^+$ occurs in the "atmospheric system", but excitation to $^3\Sigma u^-$ takes place in the "Schumann–Runge system." The energies of the two singlet oxygen molecules are 37.5 and 22.5 kcal, respectively. Occupation of the highest orbitals of the two single oxygen molecules differ in that in $^1\Delta g$ both electrons are located in the same orbitals. There are two types of reactions of O_2 ($^1\Delta g$) with chlorinated hydrocarbons: (a) the so-called "ene" reaction, and (b) the oxygenation of polycyclic compounds such as chlorinated cyclopentadienes or heterocycles which give endoperoxides (transannular peroxides) (Pitts, 1969).

The O(^{3}P) atoms also are important. They are formed mainly by dissociation of nitrogen dioxide and hence play a special role in the contaminated atmosphere. The best method to generate oxygen atoms in the ground state is the mercury-sensitized N_2O photolysis. Other possible ways of generating O(^{3}P) such as, for example, NO_2 photolysis, entail certain drawbacks because NO_2 itself can, for instance, react with the chlorinated hydrocarbon being investigated. It is for this reason that the mercury-sensitized NO_2 photolysis is preferred. Figure 9 surveys the reactions of aldrin (**1** in Fig. 9) with O(^{3}P) (Saravanja-Bozanic *et al.*, 1977). This compound reacts to form dieldrin (**3**), and there is thus a stereospecific epoxidation of the unchlorinated double bond of

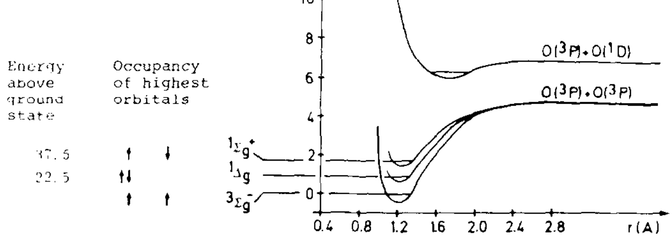


FIG. 8. Franck–Condon diagrams for various states of the oxygen molecule.

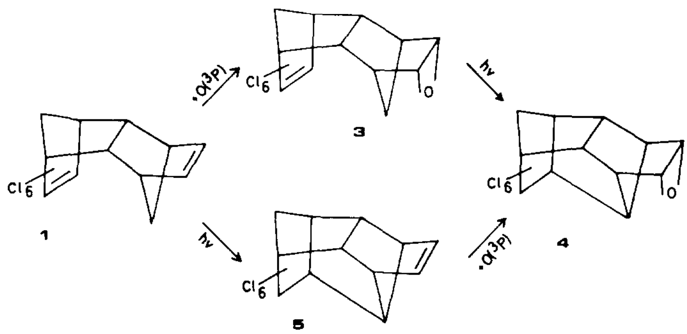


FIG. 9. Reaction of aldrin (1) with O(^{3}P).

aldrin. O(^{3}P) does not attack the chlorinated double bond. The purely photochemical reactions lead to the bridged products such as photodieldrin (**4**) and photoaldrin (**5**) whereby the unchlorinated double bond of aldrin is epoxidized further. It follows that a species of oxygen, for example O(^{3}P), can perfectly well compete with a gas-phase photoisomerization. Two directions are followed by reaction, and the dieldrin formed can be isolated as main product. Chlordene (**2**), a hexachloro-4,7-methanoindene derivative, reacts analogously (Fig. 10). Here an epoxide (**6**) is also formed stereo-

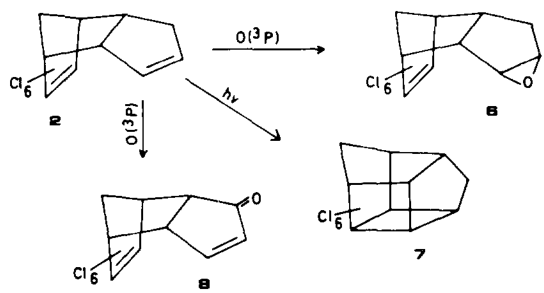


FIG. 10. Reaction of chlorden (**2**) with O(^{3}P).

specifically. This reaction competes also in this case with the intramolecularly proceeding (2 + 2)-cycloaddition leading to cage-isomers of chlordene (**7**). Formation of small amounts of 1-ketochlordene (**8**) is observed as well. This would mean that allyloxy oxidation by O(^{3}P) is possible, but whether a 1-exo-hydrochlordene is formed primarily cannot be answered negatively with 100% assurance. It is certain, though, that ground-state oxygen atoms do not react with the chlorinated bicyclo 2.2.1 heptene base structure of aldrin and chlordene. This fact is very likely attributable to the chlorine atoms, which screen the double bond and block an attack by O(^{3}P).

(3) *Photomineralization reaction.* In the search for new simulation models for the tropospheric condition studies, photocatalyzed reactions with chlorinated hydrocarbons on the interface between the solid and the gaseous phase were performed (Gäb *et al.*, 1975b). These experiments were to serve primarily as simulating reactions for those of chlorinated hydrocarbons on dust particles as well as on solid and liquid aerosols in the atmosphere. Further investigations (Gäb *et al.*, 1977; Thamm *et al.*, 1977) showed that chlorinated hydrocarbons picked as model substances were degraded to

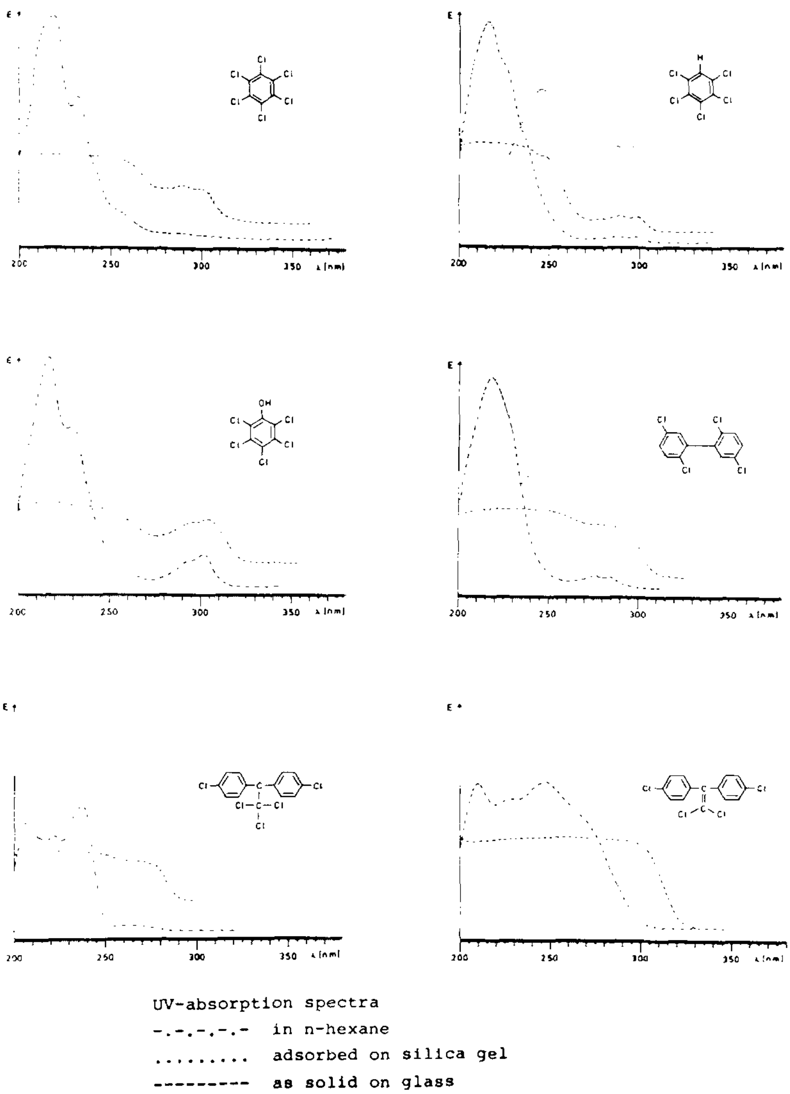


FIG. 11. The uv absorption spectra of some chlorinated aromatic hydrocarbons.

CO_2 and HCl, respectively. This unusual reaction proceeding under mild photochemical conditions led us to reflect, first, whether these reactions are also feasible for other classes of substances and, second, why it is precisely photomineralization which is accelerated in the adsorbed state. The following questions needed to be answered: (a) How does the uv behavior of these substances change when they are adsorbed? (b) Do energy transfer reactions take place between substances and oxygen molecule? (c) Which possible oxygen species can participate in the photomineralization reaction? As is well-known, the uv behavior especially of aromatics changes when they are adsorbed on active surfaces.

Figure 11 shows the uv spectra of some aromatic chlorinated hydrocarbons in

TABLE 1

ULTRAVIOLET IRRADIATIONS (λ > 290 NM) OF PENTACHLOROPHENOL, DDT, AND DDE AS SOLIDS IN AN OXYGEN STREAM (7 DAYS)

Compound	Amount employed (mg)	Amount recovered (mg)	CO_2 (mg)	HCl (mg)	Cl_2
Pentachlorophenol	80	69	15	6	—
DDT	94	89	12	2	—
DDE	98	85	10	8	—

solution when adsorbed on silica gel and as solids. The uv peaks of hexachlorobenzene recorded at 220–235 nm are displaced to 245 and 260 nm. Also, the ^1L_b band at 295 nm is much more marked than it is in solution. Pentachlorophenol and pentachlorobenzene exhibit the same behavior. In the case of pentachlorophenol the bathocromic shift of the final absorption band is 20 nm. Tetrachlorobiphenyl, DDT, and DDE show analogous bathocromic shifts which, in the case of DDE, are very clearly evident. Here the absorption produces a shift of the absorption band beyond 290 nm. This would mean that many chlorinated hydrocarbons, which normally cannot be excited in the troposphere because of their absorption, can perfectly well absorb uv light at wavelengths above 290 nm, hence making photophysical and photochemical reactions possible. On the other hand, recent experiments have shown that different oxygen species participate in the photomineralization reaction. Thus, one may assume that compounds with structural prerequisites are entirely able to generate singlet oxygen (energy transfer mechanisms between the substance and oxygen molecule on the surface). Irradiation ($\lambda > 290$ nm) of pentachlorphenol, DDT, and DDE in the presence of oxygen shows clearly that these substances are mineralized as solids. Here, pentachlorophenol is mineralized faster than DDT and DDE. Only CO_2 and HCl were detected but no Cl_2. To give a comparison with this irradiation, it is necessary to consider the results of uv irradiating the same substances in an adsorbed form. Irradiating these substances with uv ($\lambda > 290$ nm) shows clearly how rapidly these chlorinated hydrocarbons, which otherwise rank as very stable, are mineralized under simulated tropospheric conditions (Tables 1 and 2). Under the same conditions aldrin, dieldrin, photodieldrin, chlorinated olefins, some chlorinated aromatic hydrocarbons

TABLE 2

ULTRAVIOLET IRRADIATIONS (λ > 290 NM) OF PENTACHLOROPHENOL, DDT, AND DDE ON SILICA GEL (100 G) (7 DAYS)

Compound	Amount employed (mg)	Amount recovered (mg)	Photoproduct
Pentachlorophenol	102 (100%)	12 (12%)	—
DDT	385 (100%)	255 (66%)	—
DDE	362 (100%)	69 (19%)	Dichlorobenzophenone, 38 mg Trichlorobenzophenone, 7 mg

TABLE 3

PHOTOMINERALIZATION REACTIONS OF SOME CHLORINATED HYDROCARBONS

Compound	Mineralization products			
	230 nm (2–3 days)		290 nm (6 days)	
	CO_2	HCl	CO_2	HCl
Aldrin	+[a]	+	+	+
Dieldrin	+	+	+	+
Photodieldrin	+	+	+	+
Hexachlorobenzene	+	+	—	—
Pentachlorophenol	+	+	—	—
2,4,5,2′,4′,5′-Hexachlorobiphenyl	+	+	—	—
2,5,2′,5′-Tetrachlorobiphenyl	+	+	—	—
Toxaphene	+	+	—	—
2,10-Dichlorobornane	+	+	—	—
2,6-Dichlorobornane	+	+	—	—
Hexachlorobutadiene	+	+	+	+
1,1-Dichloropropene	+	+	+	+
1,2-Dichloropropene	+	+	+	+
Tetrachloroethylene	+	+	+	+
1,1-Dichloroethylene	+	+	+	+
Trichlorfluoromethane	+	+	+	+
Dichlorfluoromethane	+	+	+	+

[a] + = detected; — = not detected.

and freons are broken down to CO_2 and HCl. In contrast, hexachlorobenzene, pentachlorobenzene, toxaphen, lower chlorinated bornane derivatives, and chlorinated biphenyls require uv light ($\lambda > 230$ nm) for degradation. Table 3 surveys the results of photomineralizations reactions. It can be deduced from these experiments that the uv radiation from the sun possesses the necessary energy to break down such stable substances. Whether this fact, which is enormously important with respect to the quality of environment, also holds for other environmental chemicals will emerge following a systematic study of selected classes of substances.

REFERENCES

ANAGNOSTOPOULOS, M. L., PARLAR, H., AND KORTE, F. (1974). Isolierung, Identifizierung und Toxikologie einiger Toxaphenkomponenten. *Chemosphere* **3**, 65.

GÄB, S., COCHRANE, W. P., PARLAR, H., AND KORTE, F. (1975a). Photochemische Reaktionen von Chlorden-Isomeren des Technischen Chlordans. *Z. Naturforsch.* **30b**, 239–244.

GÄB, S., NITZ, S., PARLAR, H., AND KORTE, F. (1975b). Photomineralization of certain aromatic xenobiotica. *Chemosphere* **4**, 251–256.

GÄB, S., SCHMITZER, J., THAMM, H., PARLAR, H., AND KORTE, F. (1977). Photomineralization of organic compounds. *Nature* (London) **270**, 331.

HINES, C. O. (1965). *Physics of Earth's Atmosphere*. Prentice-Hall, Inc., Englewood Cliffs, N.J.

PARLAR, H., GÄB, S., LAHANIATIS, E. S., AND KORTE, F. (1975). Photoreversibler Wasserstofftransfer an verbrückten Chlorkohlenwasserstoffen als Konkurrenzschritt zur ($\pi\sigma \rightarrow 2\sigma$)-Reaktion. *Chem. Ber.* **108**, 3692.

PARLAR, H., GÄB, S., NITZ., S., AND KORTE, F. (1976). Zur Photochemie des Toxaphens: Reaktionen von chlorierten Bornanderivaten in Lösung und adsorbiert and Kieselgel. *Chemosphere* **5**, 333.

PARLAR, H., NITZ, S., GÄB, S., AND KORTE, F. (1977). A contribution to the structure of the toxaphene components. Spectroscopic studies on chlorinated bornane derivatives. *J. Agr. Food Chem.* **25**, 68.

PITTS, J. N. (1969). Photochemical air pollution: Singlet molecular oxygen as an environmental oxidant. In *Advances in Environmental Sciences* (J. N. Pitts and R. L. Metcalf, eds.), pp. 289–337. Wiley–Interscience, New York.

SARAVANJA-BOZANIC, V., GÄB, S., HUSTERT, K., AND KORTE, F. (1977). Reaktionen von Aldrin, Chlorden und 2,2'-Dichlorbiphenyl mit $O(^3P)$. *Chemosphere* **6**, 21–26.

SCHARF, H. D., AND FLEISCHHAUER, J. (1975). Photophysikalische und photochemische Grundlagen. In *Methoden der Organischen Chemie, Photochemie I*, pp. 1. Georg Thieme-Verlag, Stuttgart.

STEVEN, W. (1974). *Bestimmung der Quantenausbeute der Bildung des Dechlorierungsproduktes der Dichlorbenzole, Chloraniline und Chlorphenole*. Dissertation, University of Bonn.

THAMM, H., SCHMITZER, J., PARLAR, H., GÄB, S., AND KORTE, F. (1978). Photomineralisierung von Chlorbenzolen in adsorbierter Phase. Paper in preparation.