Environmental Generation and Degradation of Dibenzodioxins and Dibenzofurans

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Introduction

Chlorinated dibenzo-*p*-dioxins and dibenzofurans have been known to chemists for many years. 2,8-Dichlorodibenzo-*p*-dioxin was first reported in 1941 (*1*); the 2,3,7,8-tetrachloro- (TCDD) and octachloro- (OCDD) analogs followed in 1957 (*2*). Extensive research by Gilman (*3*) and by Pohland and Yang (*4*) provided data on many others. Likewise, simple chlorinated dibenzofurans have been reported since the early 1930's (*5*), while experience with the more highly chlorinated ones is comparatively recent (*6*, *7*).

Although the unusual toxicity of certain of these compounds was recognized at an early date through occupational illness and toxic effects on domestic animals (*8*), major concern arose only when the toxic and teratogenic properties of TCDD became apparent in widely-distributed pesticides such as 2,4,5-T (*9*, *10*). Subsequent analysis (*7*, *11*, *12*) showed that a variety of chlorinated dibenzo-*p*-dioxins and dibenzofurans can occur as impurities from the manufacture of many industrial and agricultural chemicals based on chlorophenols and certain chlorinated aromatic hydrocarbons. To cite but a single example, production statistics (*13*) suggest that at least 50 million pounds of 2,4,5-trichlorophenol and its derivatives are manufactured in the United States each year, almost all of which contains low but detectable levels of TCDD.

The dioxins are formed most directly by heating an *o*-chlorophenol or its salts above about 200°C in either the presence or absence of a solvent. For example, heating pentachlorophenol (PCP) at 300°C for 24 hr provided a low yield of OCDD [eq. (1)], while heating the sodium salt under the same conditions provided a much higher yield (*2*, *14*, *15*). Reaction of the dipotassium salt of catechol with 1, 2, 4-trichlorobenzene in dimethyl sulfoxide at 175°C produced a 70% yield of 2-chlorodibenzo-*p*-dioxin (*4*); the nitro group can serve instead of chlorine as the displaced group (*4*, *16*). Although dibenzofurans may be prepared by dehydration of 2,2'-dihydroxybiphenyls (*16*, *17*, *18*), 2-chloro-2-hydroxy- and 2,2'dichlorobiphenyls also provide them when treated with aqueous alkali (*19*, *20*), analogous to dioxin formation.

Although related reactions have been suggested to operate by a free-radical mechanism (*21*), the preponderance of evidence indicates that the above processes actually represent nucleophilic substitution (*22*, *23*). However, the C-Cl bond of the aromatic ring is much more stable than that in corresponding aliphatic compounds, and high temperatures are required to achieve reasonable reaction rates unless activating ring substituents such as nitro groups are present.

Other means can be used to activate the ring, for example the intermediacy of a

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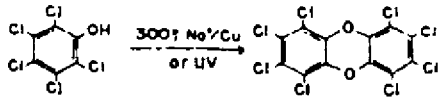
copper complex (the Ullmann reaction) (*23*). In the presence of powered copper or copper salts, a few hours at 160°C converts normally unreactive *o*-chlorophenols to dibenzo-*p*-dioxins (*3, 4, 13*). Ultraviolet light also can provide ring activation for both nucleophilic displacements and radical reaction (*24*); thus, either heat or light theoretically could transform almost ubiquitous chlorinated aromatic compounds into dioxins and dibenzofurans under environmental conditions.

Thermal Generation

Despite the suggestion (*25*) that phenol derivatives such as 2,4,5-T might be decomposed to dibenzodioxins by heat, further investigation has failed to demonstrate the conversion (*26, 27*). Actually, few circumstances are apparent in which such compounds would be subjected to both the concentration and pyrolytic conditions necessary for thermal condensation to occur; the accidental or intentional burning of herbicide-treated rangeland, for example, provides one such theoretical possibility.

However, one very real possibility does exist. A major proportion of currently produced exterior plywood and other millwork is treated with PCP, as are a number of other wood products. The burning of scrap plywood and mill wastes should provide sufficient heat and concentration to convert the fungicide into dioxins or phenoxyphenols (predioxins) whose high degree of chlorination would cause them to volatize or move with smoke rather than burn. Predioxins would be expected to form dioxins and polyphenyl ethers upon pyrolysis (*28*).

To test this concept, small chips of commercial plywood containing 53 μg/g of PCP by analysis were completely charred. The smoke and volatiles were trapped and their dioxin content compared with that of similar, solvent-extracted chips. The OCDD level in the wood was only 1 ng/g, while that in the pyrolyzate was estimated at about twice this amount, despite a persistent but nonchlorinated interference. Hepta- and hexa-



(1)

chlorodibenzo-*p*-dioxin but no TCDD were present in each sample. Identities were confirmed by gas chromatography with a mass-spectrometer detector (GC/MS).

Photochemical Generation

The ultraviolet component of sunlight is sufficiently energetic to generate free radicals by homolytic dissociation of both phenols and chlorinated aromatic compounds. The short-wavelength cutoff of ultraviolet radiation by the atmosphere is approximately 290 nm (Fig. 1), and spectral energy increases sharply above this. The homolytic dissociation energies of the Ar-Cl bond (about 80 kcal/einstein) and the ArO-H bond (about 90 kcal/einstein) correspond to wavelengths near 360 and 320 nm, respectively—clearly within the sunlight region—and free-radical mechanisms have been proposed for reactions of PCP (*29*) and other chlorophenols (*30*) in sunlight.

Blessed indeed (at least by the environmental photochemists) are those parts of the world which experience reliable, intense sunlight during most of the year. Because it varies so drastically with latitude, elevation, climate, and even the degree of air pollution, not to mention its short diurnal availability, the ultraviolet portion of solar radiation often is simulated for laboratory investigation; most of the work described here was conducted in a "sunlight-simulator" equipped with F40BL fluorescent lamps (General Electric Co.) exhibiting the spectral energy distribution also shown in Figure 1 (*31*).

It is a fundamental law of photochemistry

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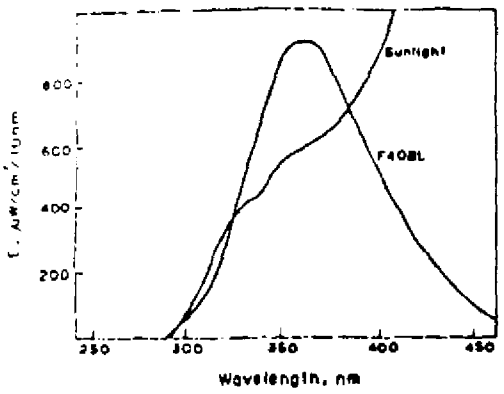

FIGURE 1. Spectral energy distribution of an F40BL fluorescent ultraviolet lamp compared with summer sunlight.

that radiation must be absorbed before reaction can occur. However, it is not necessary that the light energy absorbed by aromatic rings bring about bond scission directly. As in the previous examples, the absorption of energy can activate the ring and facilitate nucleophilic displacements. In typical photonucleophilic reactions (*24*), chloride may be displaced from 4-CPA (4-chlorophenoxyacetic acid), 2,4-D (2,4-dichlorophenoxyacetic acid), and 2,4,5-T (2,4,5-trichlorophenoxyacetic acid) by hydroxide ion to generate phenols, and, in accordance with earlier work of Munakata (*29*, *32*) we now find that PCP forms chlorinated catechols and resorcinols in aqueous media irradiated at sunlight wavelengths. In polychlorinated compounds, displacement of the chlorine *ortho* to the oxygen predominates.

Under these circumstances, it might be expected that a chlorophenate anion could attack the light-activated ring of another chlorophenol to form a diphenyl ether, and the reaction could be repeated intramolecularly to generate a chlorinated dibenzo-*p*-dioxin. Indeed, the irradiation of aqueous solutions of dioxin-free sodium PCP was found to generate OCDD, although only very small amounts could be detected by gas chromatography (*33*). Repeated attempts to detect TCDD after the irradiation of 2,4,5-T, 2,4,5-trichlorophenol, or sodium 2,4,5-trichlorophenate solution were unsuccessful.

The expected photonucleophilic formation of phenols from other aromatic halides such as chlorobiphenyls was demonstrated both with simple models (*34–37*) and with highly complex polychlorinated biphenyl (*PCB*) mixtures (Arochlors) (*36*). For example, irradiation of an aqueous suspension of 4,4'-dichlorobiphenyl provided 4-chloro-4'-hydroxybiphenyl and 4-chlorobiphenyl. However, as in the classical examples of synthesis cited previously (*19*, *20*), appropriately substituted chlorinated biphenyls also might be expected to form chlorodibenzofurans. Irradiation experiments with five pure 2-chlorinated biphenyls as 5 mg/l. aqueous suspensions, followed by resolution and examination of the products by GC/MS, showed that traces of 2-chlorodibenzofuran were detectable (eq. (2)], although only the 2,5-dichloro- and 2,5,2',5'-tetrachlorobiphenyls provided identifiable amounts (a roughly steady 0.2% yield during a 7-day irradiation).



(2)

Photochemical Degradation

Our failure to detect TCDD as a product of 2,4,5-trichlorophenol photolysis can be explained on the basis of the extreme instability of the lower chlorinated dioxins to light (*38*). In either sunlight or the sunlight-simulator, 2,7-dichloro-, 2,3,7-trichloro- and 2,3,7,8-tetrachlorodibenzo-*p*-dioxins (5 mg/l. in methanol) were entirely decomposed within a few hours (Fig. 2). However, OCDD was much more stable under these conditions, which explains why traces of it could be

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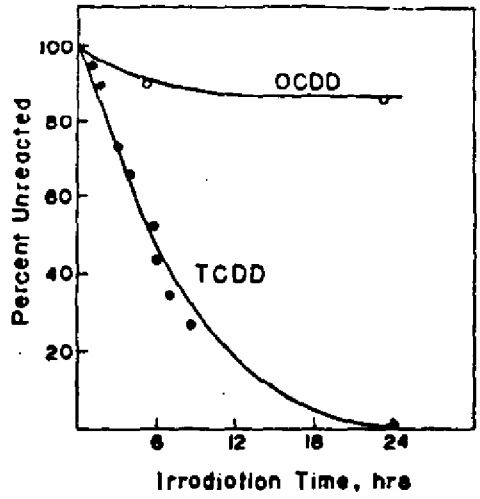
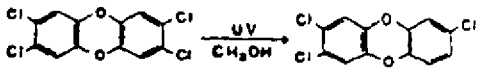


FIGURE 2. Photodecomposition rates of (○) OCDD (2.2 mg/l.) and (●) TCDD (5 mg/l.) in purified methanol under simulated sunlight (F40BL lamp).

isolated after the irradiation of PCP in water.

The rapid photodecomposition of TCDD in alcohols is accomplished by reductive dechlorination [eq. (3)], and an effective hydrogen donor appears absolutely necessary. Consequently, photoreduction in organic media proceeds efficiantly to replace halogens one at a time with hydrogen atoms; the reduction is very sluggish in water and fails entirely in thin solid films of pure TCDD or on dry, irradiated soil surfaces (*39, 40*). The mechanism has not been determined, although both the well-known free-radical hydrogen abstraction from solvent (*30, 41*) and hydride transfer (*24*) are possible. OCDD photoreduction provided detectable traces of hepta- and hexachlorodioxins, and chlorinated pesticides including 4-CPA, 2,4,5-T, PCP, PCNB (pentachloronitrobenzene), and hexachlorobenzene behaved similarly, as did the chlorinated biphenyls.

On the basis of our previous experience with dioxins, biphenyls, and the other chlorinated compounds, it came as no particular surprise that model chlorinated dibenzofurans also were photoreduced in methanol



(3)

or even in water. For example, when a 5 mg/liter methanol solution of pure 2,8-dichlorodibenzofuran was irradiated in the sunlight-simulator, 2-chlorodibenzofuran was the product detected by GC/MS, and more than 95% of the starting material was photolyzed within 48 hr (Fig. 3). However, the inadvertent use of highly purified methanol in a similar experiment revealed only very slow photolysis within the same period of irradiation. The irradiation of a more concentrated solution (10 mg/l.) in the purified solvent also indicated slow decomposition; after 90 hr, the addition of 10 mg/l. of 4,4'-dichlorobenzophenone as a photosensitizer resulted in a sharp increase in the photolysis rate, although acetone did not appear to sensitize the photolysis in this instance. It appears, then, that impurities in common solvents can drastically alter photodecomposition rates.

Discussion

A remarkable level of scientific attention recently has been devoted to the chlorinated dibenzodioxins and dibenzofurans. From the smattering of articles representing the four decades preceding 1970, two recent conferences (*42, 43*) alone have provided more than 60 research papers. While earlier work dealt largely with basic chemistry and occupational health, more recent concerns have been primarily associated with the possible environmental occurrence and environmental effects. Indeed, much of the current effort to understand and control these compounds arose because of unanswered questions about their environmental impact on humans, domestic animals, and wildlife.

Although improved manufacturing and

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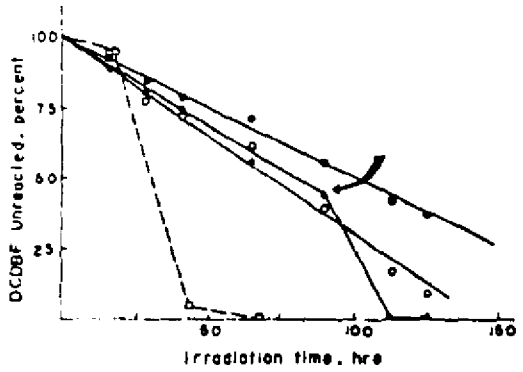

FIGURE 3. Photodecomposition rates of 2,8-dichlorodibenzofuran (DCDBF): (●,▲) in acetone-free methanol (10 mg/l.); (○) in acetone-free methanol containing added acetone (820 mg/l.); (□) in laboratory-grade methanol. The arrow indicates addition of 10 mg/l. of 4,4'-dichlorobenzophenone. Straight lines drawn for comparison only.

surveillance methods have dramatically reduced dioxin and dibenzofuran levels among industrial chemicals (*18*), there is evidence that under idealized conditions, at least, both types of compounds can be generated from commonly used chlorophenols and chlorinated biphenyls under environmental conditions. The driving force can be either the ultraviolet component of sunlight impinging upon thin films, surfaces, or solutions or heat such as might be encountered in burning wood. Conceivably but not demonstrably, phenol derivatives such as the phenoxy herbicides also might provide the raw material, but, in any case, the necessary generative reactions clearly have been demonstrated.

On the other hand, environmental persistence or accumulation theoretically could be balanced by the simultaneous destructive action of light or heat. Photolysis can be rather rapid under idealized conditions, although a hydrogen donor appears to be required, and OCDD is rather stable compared to the highly toxic TCDD. The charring temperature of wood (>350°C) is well above that frequently reported to convert PCP into OCDD, but the thermal stability of the dioxins has not been reported.

Just how probable are the environmental formation and decomposition of dibenzodioxins and dibenzofurans? The ultraviolet component of sunlight undoubtedly is capable of energizing their degradation in the presence of organic hydrogen donors, and those donors can be expected to be present at and after the time of application as either the usual formulation solvents (such as xylene or petroleum hydrocarbons), as active constituents of the formulation (for example, the alkyl esters of 2,4-D and 2,4,5-T), or as natural organic films. Although TCDD has been reported to be stable to irradiation on soil surfaces, it was not accompanied in those experiments by a nonvolatile organic source of hydrogens as it would be in the field. It was quite stable, too, when suspended in water but rapidly degraded when benzene also was present (*39*).

Photosensitization also must be an important consideration, as demonstrated by the effect of dichlorobenzophenone on the photoreduction of chlorinated dibenzofurans. Such sensitizers have been shown to be expected under field conditions (*44–46*) and could drastically increase the photolysis rates of xenobiotics. At the least, photochemical investigations in the laboratory should recognize the possibility of sensitization, for example by impurities commonly present in even purified grades of methanol. All together, degradation appears to outrace generation in most of our laboratory studies.

However, the same solvents and active ingredients which could act as hydrogen donors and sensitizers also could protect dioxins and dibenzofurans from photolysis under practical conditions. For example, while light absorption by TCDD might be only partially obscured by the absorption of a 2,4,5-T formulation (Fig. 4) and chlorinated dibenzofurans would be little shielded by PCBs (Fig. 5), the low level of OCDD in a technical formulation of PCP or sodium PCP should remain well-protected from light (Fig. 6), although an improved, low-dioxin product (Dowicide EC-7) was somewhat less opaque. Clearly, too, OCDD is environmental-

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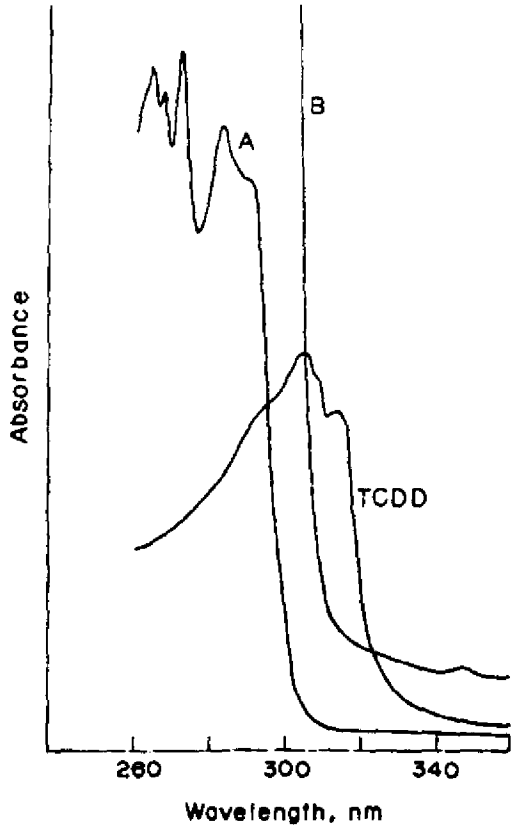

FIGURE 4. Ultraviolet absorption spectra of two concentrations (A,B) of commercial brush-killer (25.1% 2,4-D isooctyl ester and 12.0% 2,4,5-T isooctyl ester in aromatic hydrocarbon solvent) in methanol compared with that of TCDD.

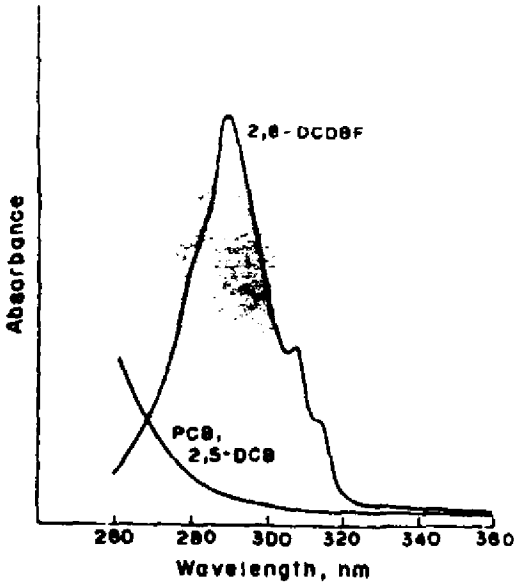

FIGURE 5. Ultraviolet absorption spectra of PCB (Arochlor 1254) and 2,5-dichlorobiphenyl in methanol compared with that of 2,8-dichlorodibenzofuran (2,8-DCDBF).

ly generated—especially by heat—albeit inefficiently.

Considering the probable photolysis of TCDD to nontoxic products and the insignificant rate of dibenzofuran formation from biphenyls, it is hardly surprising that they remain undetected in environmental samples. In fact, OCDD and its immediate toxic reduction products—the hexa- and heptachlorodioxins—emerge to be of even more environmental health interest. For example, they appear to be the best candidates for both photochemical formation and stability; obviously, they are released by heat from common materials of construction; and the relatively innocuous OCDD readily undergoes reduction to form less chlorinated homologs which are both rather stable and toxic (47).

But are these compounds released, in fact? Are chlorinated dibenzo-*p*-dioxins and dibenzofurans actually generated and destroyed out there in the real world? Regrettably, no one seems to know. Experiments such as we have described generally are conducted under idealized conditions: pure compounds and solvents, artificial substrates, and even artificial sunlight. What of the sensitizers and sunscreens, the hydrogen donors and competing nucleophiles which must be present in actual environmental applications? It is apparent that rather large stakes in terms of biological research investments, manufacturing, and public health now are riding on what previously may have seemed to be only exotic details of xenobiotic chemistry.

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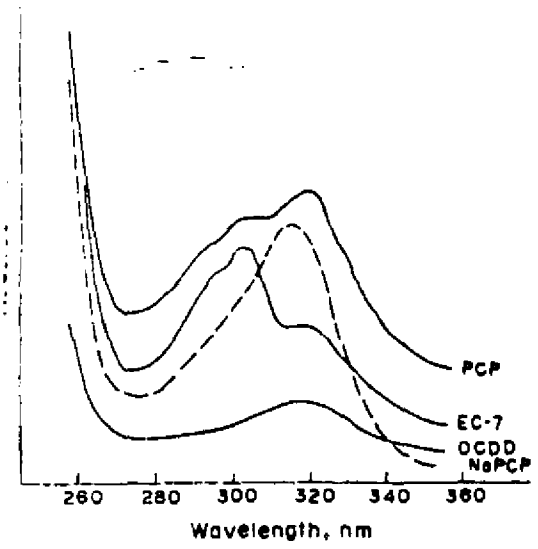

FIGURE 6. Ultraviolet absorption spectra of commercial PCP (35.3% PCP and 4.1% other chlorinated phenols in petroleum distillate) and Dowicide EC-7 (88% PCP and 12% 2,3,4,6-tetrachlorophenol) in methanol and commercial NaPCP (80-85% sodium pentachlorophenate) in water compared with that of OCDD in methanol.

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