Photodecomposition of Chlorinated Biphenyls and Dibenzofurans

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The polychlorinated biphenyls (PCB's) have been widely detected throughout the world's aquatic environments (DUKE et al. 1970, VIETH and LEE 1970, SCHMIDT et al. 1971, HARVEY et al. 1973). They are accumulated by aquatic organisms (DUKE et al. 1970, ZITKO 1970, RISEBROUGH and de LAPPE 1972, STALLING and MAYER 1972) and so present concern not only for their acute and chronic toxic effects (DUKE et al. 1970, ZITKO 1970, HANSEN et al. 1971, STALLING and MAYER 1972) but also because of the probability of their transmission in food chains.

PCB's do not appear to be particularly toxic to higher animals (PANEL 1972). In fact, several effects including chloracne, hepatotoxicity, and prophyria originally attributed to PCB exposure later were ascribed to contained chlorinated dibenzofurans (PANEL 1972, KIMBROUGH 1972). Although toxicity measurements with pure PCB isomers appear not to have been reported, limited data with Arochlors indicate that maximum acute toxicity resides in the di-, tri-, and perhaps tetrachloro compounds (MORGAN 1972, STALLING and MAYER 1972, MAYER 1973).

The chlorinated biphenyls, like chlorinated hydrocarbon insecticides, are highly hydrophobic and may be expected to occur in lipid phases such as the organic films sometimes found on the surface of natural waters (DUCE et al. 1972). However, the aqueous solubility of the lower chlorinated members is surprising; water saturated with the commercial Arochlor 1221 was claimed (ZITKO 1970) to contain 5 mg/liter, although other data indicate lower values (PANEL 1972).

Recent laboratory investigations (MOILANEN and CROSBY 1973) show that DDT and DDE are converted, in part, to di-, tri-, and tetrachlorobiphenyls under simulated atmospheric irradiation conditions; these biphenyls would be expected to precipitate in rainfall (TARRANT and TATTON 1968) if they were to form in the atmosphere or be selectively volatilized from surfaces. Consequently, the possible degradative effects of the ultraviolet (UV) component of sunlight on the low-molecular weight PCB isomers is of particular interest and was the subject of this investigation.

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Materials and Methods

Materials. Pure standards of chlorinated biphenyl isomers were purchased from Aldrich Chemical Co. (Milwaukee, Wisc.) and Analabs, Inc. (North Haven, Conn.) and were homogeneous upon gas chromatography (glc). 2-Chloro- and 2,8-dichlorodibenzofuran were prepared by the method of GILMAN *et al*. (1934). Methanol was redistilled reagent-grade and acetone-free (Mallinckrodt Chemical Co.), and other reagents were pure grades used as received.

Irradiation. The chlorinated biphenyl (1 or 10 mg/l) in a small volume (0.3-2 ml/l) of methanol was suspended in distilled water; one liter of suspension was held in the dark, while another was irradiated for 15-26 summer days in Davis, Calif., or for 1-2 weeks in an aerated, sunlight-simulating, laboratory photoreactor (CROSBY and TANG 1969). The suspensions were extracted exhaustively with benzene, the extracts dried and vacuum-evaporated to 0.5 ml, and aliquots subjected to glc after methylation with ethereal diazomethane.

The chlorinated dibenzofurans were dissolved in purified methanol (10-100 mg/l) and irradiated in the photoreactor. Aliquots were removed at intervals and subjected directly to glc.

Chromatography. The biphenyls were chromatographed on a 180 x 0.2 cm column of 2% Carbowax 20M on 60/80 Chromosorb G, temperature-programmed 150-250°C at 10°C/min, TC detector. Fractions were collected from the effluent gas in glass capillary tubes, purified by rechromatography, and their spectra compared with those of authentic specimens where possible.

For mass spectrometry, the collected fractions were rechromatographed on a 180 x 0.2 cm column of 2% OV-1 on 60/80 Chromosorb G, temperature-programmed 150-250°C at 10°C/min, and detected with a Finnigan Model 3000 mass spectrometer detector (GC/MS).

The dibenzofurans were chromatographed on a similar 5% SE-30 column at 195°C (EC detector) or 5% XE-60 at 190° (FID detector).

Results and Discussion

Previous work in this laboratory demonstrated that chlorinated aromatic compounds are reductively dechlorinated readily in organic solvents when irradiated with UV light at sunlight wavelengths (CROSBY and HAMADMAD 1971). Under similar conditions, irradiation in aqueous media results in replacement of the chlorine by hydroxyl as well as by hydrogen (CROSBY and LEITIS 1969, MOILANEN and CROSBY 1972).

Several authors (SAFE and HUTZINGER 1971, HERRING *et al*. 1972, HUSTERT and KORTE 1972, HUTZINGER *et al*. 1972, RUZO *et al*. 1972) recently have reported that simple chlorinated biphenyls as well as the complex PCB mixtures of commerce likewise underwent photoreduction in hexane solution. In aqueous suspension, our irradiation experiments also showed dechlorination (Table I);

TABLE I

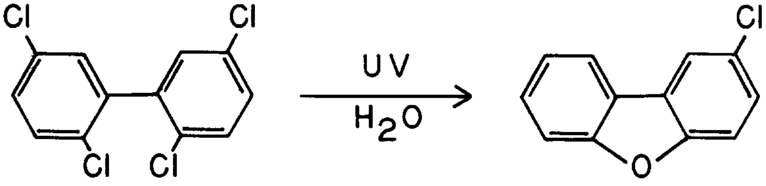
Photolysis of Chlorobiphenyls in Water

Chlorobiphenyl[a]	Irradiation[b] (hrs) A	Irradiation[b] (hrs) B	Reduced Product (m/e)	Hydroxylated Product[c] (m/e)
2,4-Cl_2	312	135	none	218
2,5-Cl_2	189	180	188	218[d]
3,4-Cl_2	192	135	none	none
4,4'-Cl_2	168	135	188	218
2,4,5-Cl_3	240	135	none	none
2,2',3,3'-Cl_4	216	235	257	287
2,2',4,4'-Cl_4	264	235	none	none
2,2',5,5'-Cl_4	168	200	257	287[d]

[a] 10 mg/l suspension indoors, 1 mg/l outdoors.
[b] F40BL lamp (A) or summer sunlight, Davis, Calif. (B).
[c] Methylated.
[d] 2-Chlorodibenzofuran detected by GC/MS.

for example, 4,4'-dichlorobiphenyl formed 4-chlorobiphenyl and 4-chloro-4'-hydroxybiphenyl, as expected, although at a relatively slow rate. The higher chlorinated isomers and polymers reported previously (HUSTERT and KORTE 1972, HUTZINGER _et al_. 1972) were not observed, and in each instance only a reduced product containing one less Cl and a single (unidentified) product with Cl replaced by OH were detected by GC/MS. Indoor and outdoor results were identical.

Treatment of 2,2'-dichloro- or 2-chloro-2'-hydroxybiphenyl with aqueous base, or simply boiling 2,2'-dihydroxybiphenyls with water, is known to form dibenzofurans (CULLINANE _et al_. 1934, ZAHN and SCHIMMELSCHMIDT 1940, CASE and SCHOCK 1943), and the photochemical formation of dibenzofurans from 2-chlorobiphenyls represented a logical extension. Irradiation of chlorinated biphenyls dispersed in water (Table I), followed by GC/MS, revealed identifiable traces of 2-chlorodibenzofuran as a photolysis product of 2,5-dichloro- and 2,2',5,5'-tetrachlorobiphenyl in roughly a 0.2% steady-state yield.



Similar irradiation of 2,8-dichlorodibenzofuran also resulted in slow dehalogenation, explaining the previous appearance of 2-chlorodibenzofuran. Irradiation in purified methanol under conditions similar to those which resulted in the rapid photoreduction of 2,7-dichlorodibenzo-p-dioxin (CROSBY et al. 1971) likewise caused disappearance of the dichlorodibenzofuran (Fig.1); like the 4-chlorobiphenyl (RUZO et al. 1972), the 2-chlorodibenzofuran remained almost unaffected by light. Decomposition in aqueous suspension was slow.

Although the environmental conversion of Arochlor constituents to dibenzofurans was predicted (RISEBROUGH and BERGER 1971), other investigators (HUTZINGER et al. 1972, MARTIN et al. 1972) have been unsuccessful in detecting the conversion of chlorinated biphenyls to dibenzofurans in light, perhaps due to the rapid decomposition under energetic (254 nm) irradiation conditions or the presence of sensitizers. The addition of the photosensitizer 4,4'-dichlorobenzophenone to a methanol solution of 2,8-dichlorodibenzofuran during irradiation (Fig.1) resulted in a sharp increase in the photolysis rate. Both natural and synthetic photosensitizers have been shown to affect other xenobiotics (LYKKEN 1972, ROSS and CROSBY 1973), and the environmental sensitization of dibenzofuran photolysis seems quite plausible.

The photodecomposition of the lower chlorinated PCB isomers in both polar and nonpolar solvents reveals the operation of environmental mechanisms which could effectively degrade these widespread contaminants. The recent report (HARVEY et al. 1973) that PCB mixtures occur dispersed in seawater at levels up to 150 ng/l indicates appropriate conditions for hydroxylation and dibenzofuran formation in addition to the probability of reductive dechlorination by organic matter in the sea. Indeed, the notable absence of the lower chlorinated biphenyls from most environmental samples (PANEL 1972) is suggestive of an important role of photodecomposition in the environmental fate of PCB's, the interpretation of their source and movement, and prediction of toxic effects on aquatic life.

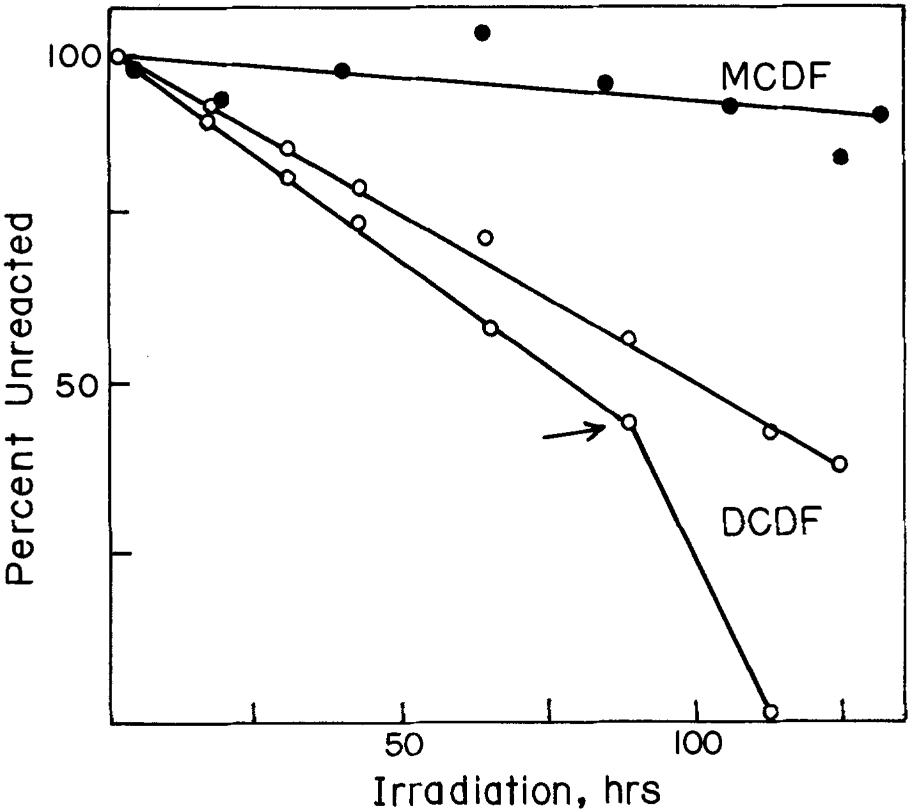


Fig. 1. Photodecomposition rates of 2-chlorodibenzofuran (MCDF) and 2,8-dichlorodibenzofuran (DCDF) in methanol at 30°C. 4,4'-Dichlorobenzophenone added as sensitizer (arrow).

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