

Photochemical Degradation of Di- and Octachlorodibenzofuran

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Introduction

In the last few years, it has been shown that polychlorinated biphenyls undergo decomposition on irradiation with artificial ultraviolet light sources and sunlight (1-7). Reductive dehalogenation of one or more chlorine atoms was a major reaction, particularly in hydrocarbon solvents. In fluorocarbon solvents or thin films, small quantities of chlorobiphenyls with increased chlorine content could also be detected. Irradiation in hydroxylic solvents gave the dechlorinated species as well as photoproducts containing oxygen. In addition, chlorinated terphenyls and quaterphenyls were also detected in some instances, and on prolonged irradiation polymeric products were formed.

It has been speculated for some time that chlorodibenzofurans may be formed from chlorobiphenyls under photochemical conditions which lead to oxygenated products. Although no chlorodibenzofurans could be detected in a number of chlorobiphenyl samples which had been exposed to sunlight for over 2 months (4), preliminary results indicated the formation of chlorodibenzofur-

ans from 2,2',4,4',6,6'-hexachlorobiphenyl in model experiments (irradiation in methanol) (8).

The toxicity of pure chlorodibenzofurans has not been thoroughly investigated (9) but appears to be higher by several orders of magnitude than that of the chlorobiphenyls, which gives this reaction particular significance.

In this regard, the photochemical behavior of chlorodibenzofurans themselves becomes of interest from the point of view of products formed (decomposition to less toxic products) and stability. As an approximation [eq. (1)], it appears that if chlorodibenzofurans are formed from chlorobiphenyls in the environment by photochemical reaction, accumulation will be a problem if $k_1 > k_2$.

Chlorobiphenyl $\xrightarrow{k_1}$ chlorodibenzofuran $\xrightarrow{k_2}$ decomposition products (1)

Since a good selection of chlorodibenzofurans is not available, only preliminary investigations with two representatives, one of low (2,8-dichlorodibenzofuran) and one of high chlorine content (octachlorodibenzofuran) are reported.

Equipment and Methods

Chemicals

2,8-Dichlorodibenzofuran (10) and octachlorodibenzofuran (11) were prepared by

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literature methods. Samples for the initial experiments were provided by Dr. A. E. Pohland, (FDA, Washington, D.C.)

Irradiations

For the irradiations in solution (450 ml hexane or methanol), a Rayonet (the Southern New England Ultraviolet Co.) photochemical reactor equipped with 16 RPR-3100 lamps (310 nm) was used. Aliquots (25 ml) were taken at times specified in Figure 1. For mass spectrometric analysis of the photolysis mixture, 2,8-dichlorodibenzofuran and octachlorodibenzofuran were irradiated in methanol for 20 min.

Thin films (50 mg) of the chlorodibenzofurans coated on the inside of quartz tubes (length: 25 cm; diameter, 4 cm) were exposed to sunlight for 10 weeks in the presence of water (2 ml) during July–September 1972. Total duration of bright sunshine

was ca. 580 hr (Meteorological Services, Canadian Forces Base, Shearwater, N. S., private communication).

Instruments

Quantitative data were obtained with a Packard model A7901 instrument equipped with 6 ft × 4 mm columns packed with either 4% SE-30 (for the 2,8-dichlorodibenzofuran) or 3% OV-210 (for the octachlorodibenzofuran) on Chromosorb W.

A DuPont/CEC 21-110B double focussing mass spectrometer was used for obtaining spectra by direct introduction. The probe was heated carefully, and spectra were recorded as the temperature was raised from 20°C to ca. 180°C.

Analysis of Samples

Quantitative analyses (photochemical stability of chlorodibenzofurans) were carried out by gas chromatography (GC) with electron capture detection on the aliquots taken from the photochemical reactor.

For the characterization of products formed, the solvent was removed from the samples and the residue chromatographed on Merck silica thin-layer plates (F-254; 0.25 mm thickness). The solvent used was hexane. For the mass spectroscopic analysis, small fractions of the total sample were transferred to a mass spectrometer sample tube. Samples from the quartz tubes were dissolved in benzene–acetone and treated as described above.

Results and Discussion

The correct numbering of the dibenzofuran ring system (Chemical Abstracts and Ring Index) is shown in Figure 2.

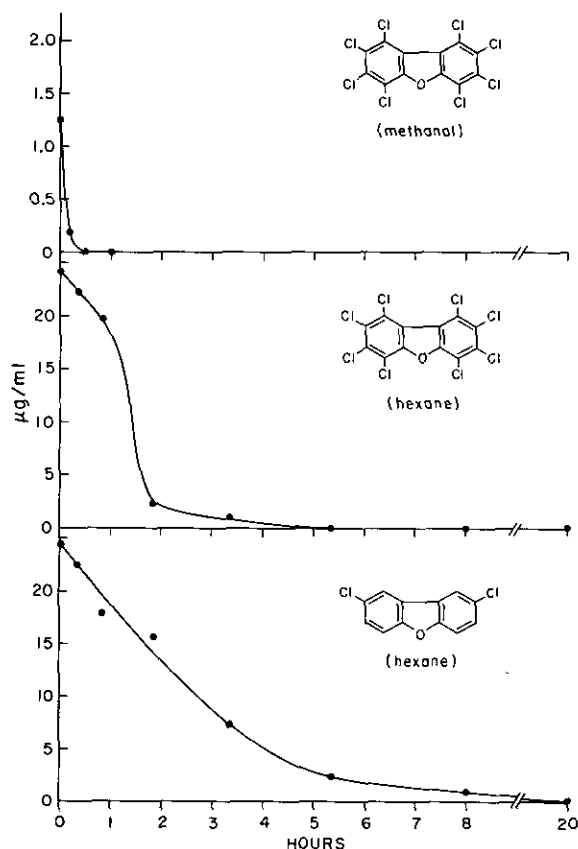


FIGURE 1. Photochemical degradation of chlorodibenzofurans in solution. Irradiation wavelength 310 nm.

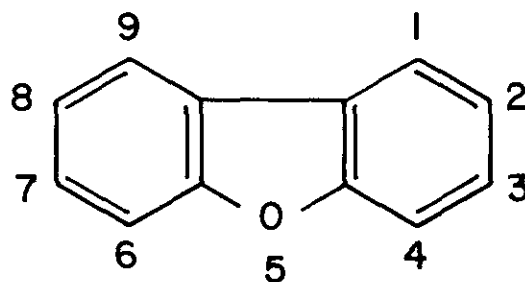


FIGURE 2. Numbering of the dibenzofuran nucleus.

Some older systems are still in use occasionally. Calculated molecular weights ($Cl = 35$) for dibenzofuran and its chlorine substitution products are given in Table 1.

Table 1. Molecular weights for chlorodibenzofurans (monoisotopic formula; $Cl = 35$)

Formula	Molecular weight
$C_{12}H_8O$	168
$C_{12}H_7ClO$	202
$C_{12}H_6Cl_2O$	236
$C_{12}H_5Cl_3O$	270
$C_{12}H_4Cl_4O$	304
$C_{12}H_3Cl_5O$	338
$C_{12}H_2Cl_6O$	372
$C_{12}HCl_7O$	406
$C_{12}Cl_8O$	440

Irradiation of 2,8-Di- and Octachlorodibenzofuran in Solution

The relative rate of decomposition of 2, 8-di- and octachlorodibenzofuran is shown in Figure 1. From these results and from the mass spectra of samples which were irradiated for 20 min it is evident that decomposition is faster in methanol than in hexane. In contrast to the chlorinated dibenzo-*p*-dioxins, where the degradation of the octachloro derivative on irradiation in methanol solution is much slower than that

of the 2,7-dibenzo-*p*-dioxin (12), the di- and octachlorodibenzofurans show similar rates of decomposition.

For the analysis of products formed, samples which were irradiated for 20 min in methanol (short exposure) and for ca. 20 hr in hexane (long exposure) were chosen.

Thin-layer chromatography of the samples exposed for 20 min showed only two spots, a relatively weak one on the origin and a large spot with an R_f similar to those starting materials ($R_f = \text{ca. } 0.55$ for 2,8-dichlorodibenzofuran; $R_f = \text{ca. } 0.75$ for octachlorodibenzofuran).

Since organochlorine compounds which give very strong molecular ions can be analyzed by mass spectrometry in mixtures (13-15), samples of the irradiated products were carefully heated in the mass spectrometer probe and spectra recorded at different temperatures. Typical spectra are shown in Figures 3 and 4. No other products but those formed by dechlorination of the corresponding chlorodibenzofuran were found to be present.

No useful mass spectra could be obtained for the yellow gum which resulted from the 20-hr irradiation experiments. A large number of peaks was observed and no recognizable chlorine isotope pattern was apparent.

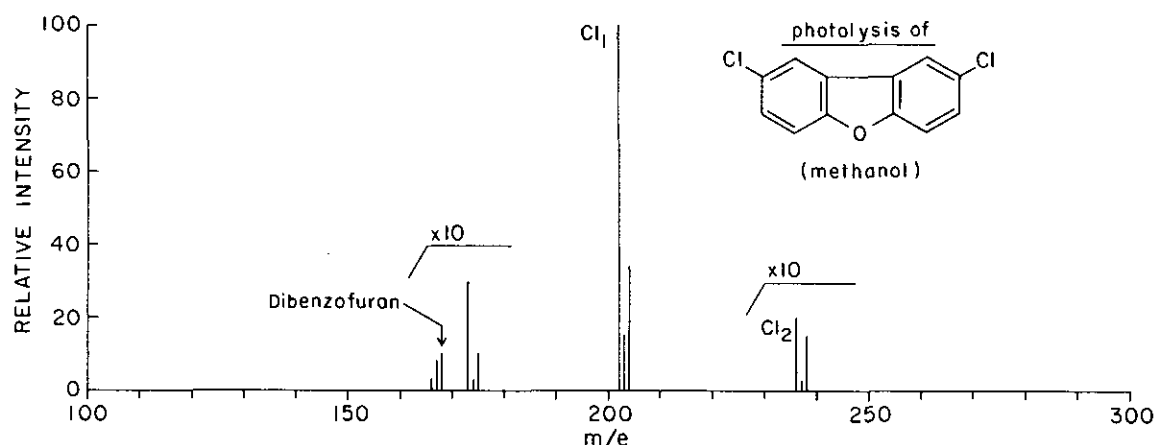


FIGURE 3. Mass spectrum (70 eV) of 2,8-dichlorodibenzofuran photolysis mixture (310 nm; 20 min; solvent methanol). Probe temperature: 40° C.

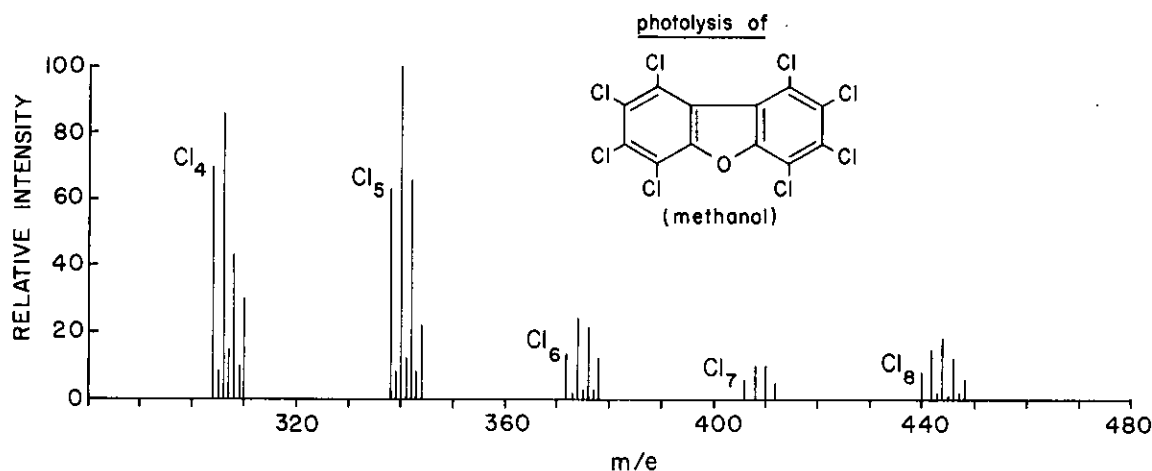


FIGURE 4. Mass spectrum (70 eV) of octachlorodibenzofuran photolysis mixture (310 nm; 20 min; solvent; methanol). Probe temperature: 80° C.

Exposure of 2,8-Di- and Octachlorodibenzofuran as Thin Film to Sunlight

The analysis by mass spectrometry was carried out as described above. Reductive dechlorination of octachlorodibenzofuran was observed to a much lesser degree than in solution. 2,8-Dichlorodibenzofuran gave, in addition to a monochloro derivative, a trichlorodibenzofuran (M^+270).

A summary of the results of the photolysis experiments in solution and thin films is shown in Figures 5 and 6.

Summary and Conclusions

Photolysis of 2,8-di- and octachlorodibenzofuran in methanol and hexane solutions results in rapid dechlorination of the substrates with the eventual accumulation of

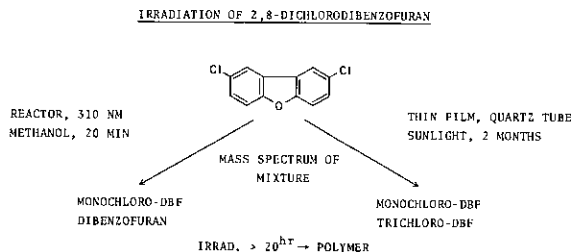


FIGURE 5. Summary of results from 2,8-dichlorodibenzofuran irradiation experiments.

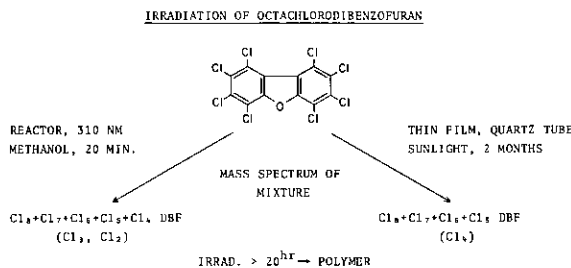


FIGURE 6. Summary of results from octachlorodibenzofuran irradiation experiments.

unidentified resinous polymeric products. Dechlorination is also observed to a certain extent when thin films of these compounds were exposed to sunlight.

These preliminary data do not allow direct comparison of dibenzofuran degradation rates with rates of photochemical formation from corresponding chlorobiphenyls (8). In view of the photochemical lability of chlorodibenzofurans, however, it seems unlikely that accumulation of these compounds formed from chlorobiphenyls by photochemical reaction in the environment will occur.

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