

COMPARATIVE RATES OF PHOTOLYSIS OF POLYCHLORINATED DIBENZOFURANS IN ORGANIC SOLVENTS AND IN AQUEOUS SOLUTIONS

Dung, M.^A, O'Keefe, P.W.^{A,B}

^ANew York State Department of Health, Albany, NY 12201, USA

^BSchool of Public Health, SUNY, Albany, NY 12201, USA

INTRODUCTION

There are several reports in the scientific literature describing the photodecomposition of polychlorinated dibenzo-p-dioxins (PCDDs) in organic solvents exposed to either sunlight or artificial light sources¹. The photodecomposition of polychlorinated dibenzofurans (PCDFs) has been less extensively investigated¹. In general reaction rates for both PCDDs and PCDFs are rapid (half-lives of minutes to hours) in hydrogen donor solvents such as hexane although photodechlorination may be a relatively minor decomposition pathway².

Acetonitrile/water mixtures have been used to study the photodecomposition of PCDDs in an aqueous medium since these compounds are relatively insoluble in pure water. Reaction rates in the acetonitrile/water mixtures are considerably slower than the reaction rates in either hexane or natural waters³.

It is possible to prepare aqueous solutions of compounds with low water-solubility by pumping water through "generator columns" containing particles coated with a thin film of the compound. The objective of this study was to compare the rates of photolysis of three PCDFs (1,2-; 1,2,7,8- and 2,3,7,8-) dissolved in organic solvents with the photolysis rates of the same compounds dissolved in pure or natural waters by means of generator columns. Experiments were carried out in sunlight and in a photochemical reactor equipped with low pressure mercury lamps emitting radiation at 300 nm.

METHODS

(I) Preparation of Generator Columns

Approximately 30 μg of a PCDF compound were dissolved in 50 ml hexane in a 100 ml round-bottomed flask to which 6 g of 0.2 mm diameter glass beads were added. The solvent was evaporated slowly using a rotary evaporator on a water bath at 40 °C. The coated beads were then added to a 8 mm id x 10 cm glass column using uncoated beads to eliminate void spaces in the column. High-purity HPLC grade water was pumped through

the column at a rate of 0.5 to 1 ml/min using a Waters HPLC pump. Concentration levels of the PCDD/PCDF compounds approaching the limit of solubility were attained after 200 to 300 ml of water had been collected. However, water was frequently collected prior to this point if the PCDD/PCDF compound could be detected at a concentration below its solubility limit.

(II) Photodegradation of PCDD/PCDF Compounds

Low-Pressure Mercury Lamps in a Rayonet Photoreactor. The Rayonet reactor (The Southern New England Ultraviolet Co.) was equipped with 12 RPR-3000 low-pressure mercury lamps which emit light in a narrow band centered at 300 nm. A Corex (DuPont Co.) centrifuge bottle containing the PCDD/PCDF compound dissolved in 150 ml organic solvent or water was placed in the center of the reactor and stirred during irradiation with a magnetic stirring bar. The reactor was allowed to reach its equilibrium temperature of 39 °C before starting a photolysis experiment and the Corex bottle was also equilibrated at the same temperature. The intensity of light at 300 nm was measured using a 0.006M potassium ferrioxalate chemical actinometer solution in a Corex bottle.

The Corex glass (2 mm thickness) can transmit 80% of UV light at 290 nm.

Sunlight Exposures. The bottles were placed horizontally in a tray covered with aluminum foil to reflect the sunlight. Exposures were carried out between 9 am and 4 pm each day.

Analyses. Aqueous solutions were extracted with four 40 ml volumes of benzene and concentrated to 100 μ l using a combination of refluxing and nitrogen evaporation. Two μ l aliquots were analyzed by a Hewlett-Packard 5970 Mass Selective Detector coupled to a 15 m DB 5 capillary column, using selected ion monitoring for the detection of PCDFs and full scan MS for the detection of unknown compounds.

RESULTS AND DISCUSSION

Photolysis rates of the PCDFs in organic solvents and aqueous solutions were found to follow first-order reaction kinetics:

$$\ln(C_t/C_0) = -kt$$

where C_0 and C_t are the concentrations of the PCDF at times 0 and t respectively and k is the photolysis rate constant. The slope of a linear plot of $\ln(C_t/C_0)$ versus time gave the photolysis rate constant.

The photolysis rate constants of 2,3,7,8- and 1,2,7,8-tetra CDFs in hexane are shown in Table 1. Since 1,2,7,8-tetra CDF is present as a contaminant in 2,3,7,8-tetra CDF and vice-versa it was possible to determine the photolysis rate constants for both isomers in the same experiment. It is apparent from the data in Table 1 that, in ultra-high purity hexane (Mallinckrodt and Baker "Capillary" grade), the photolysis rate of 1,2,7,8-tetra CDF is 1.35 times faster than that the photolysis rate of 2,3,7,8-tetra CDF and it was also found to be 1.5 times faster than the photolysis rate of 2,7-di CDF. These results can be contrasted with

results from the photolysis of PCDD compounds in organic solvents where it has been found that lower chlorinated isomers are photodecomposed more readily than higher chlorinated isomers and isomers with chlorine substituents at the lateral (2,3,7 and 8) positions are more photoreactive than peri (1,4,6 and 9) substituted isomers¹. When the PCDFs were dissolved in hexane with lower purity specifications (Baker Resi-Analyzed) the photolysis rates were considerably enhanced if the solvent had been stored for more than 4 years after manufacture.

It has been pointed out in several studies that dechlorination can account for only a small percentage of the total amount of a PCDD/PCDF compound decomposed by photolysis. However high percentages (70% and 50% respectively) of 1,2,7,8- and 2,3,7,8-tetra CDF are converted to triCDFs suggesting that dechlorination is a major pathway for the photodecomposition of tetra CDF isomers in ultra-high purity hexane. In the lower grade hexane dechlorination could account for only 10% of the losses of the tetra CDFs, suggesting that impurities in the lower grade hexane are sensitizing decomposition by pathways other than dechlorination.

Results from our experiments showed that the photolysis rate (1.26/hr) of 2,7-di CDF in pure water in the photoreactor was 20,15 and 13 times faster than in 60% acetonitrile/water, methanol or hexane respectively. Since the hydrogen donor potential of water is lower than that of hexane, methanol or acetonitrile/water, the photodecomposition of 2,7-di CDF in pure water must be occurring by a mechanism different from that found in organic solvents. For this reason acetonitrile/water probably should not be substituted for water when measuring the photolysis rate of 2,7-di CDF in water. In the case of 2,3,7,8 and 1,2,7,8 -tetra CDF, photolysis experiments in HPLC water were carried out in both a Corex centrifuge bottle and a quartz cell (Table 2). The expected order of reactivity was found in the experiments carried out using the quartz cell and the rate constants in this cell were higher than those found using the Corex bottle. The differences in reaction rates between the two cells can be explained by the higher transmission of light through quartz at wavelengths below 300 nm.

The photolysis rates of the two tetra CDF isomers were enhanced by factors of 2 when they were dissolved in either Hudson River water or Saratoga Lake water instead of pure water (Table 2). There was minimal enhancement (<10%) of the photoreactivity of the 2,7-di CDF by the natural waters. As in the case of other pollutants natural organics in the water may be acting as photosensitizers.

REFERENCE

- 1 Choudhry GH, Webster, GR. Environmental Photochemistry of Polychlorinated Dibenzofurans (PCDFs) and Dibenzo-p-dioxins (PCDDs): A Review. *Toxicol. Environ. Chem.* 1987;14:43-61.
- 2 Kieatiwong S, Nguyen LV, Herbert VR, Hackett M, Miller GC, Mille MJ, Mitzel R. Photolysis of Chlorinated Dioxins in Organic Solvents and Soils. *Environ. Sci. Technol.* 1990;24:1575-1580.
- 3 Friesen KJ, Vilks J, Muir DCG. Evidence of Sensitized Photolysis of Polychlorinated Dibenzo-p-dioxins in Natural Waters under Sunlight Conditions. *Chemosphere* 1990;20:27-32.

Table 1. Rate Constants and Half-Lives for the Photodecomposition of TetraCDF Isomers Exposed in Organic Solvents to 300 nm Radiation.

Solvent	Rates Constants and Half-Lives			
	2,3,7,8-tetraCDF		1,2,7,8-tetraCDF	
	k (hr ⁻¹)	$t_{1/2}$ (hr)	k (hr ⁻¹)	$t_{1/2}$ (hr)
Hexane (high purity)				
Mallinkckrodt	$1.05 \times 10^{-1*}$	6.6	1.37×10^{-1}	5.1
Baker Capillary	$1.02 \times 10^{-1*}$	6.8	1.40×10^{-1}	5.0
Baker Resi	$1.10 \times 10^{-1*}$	6.4	1.57×10^{-1}	4.5
Baker Resi	1.47×10^{-1}	4.7	$1.84 \times 10^{-1*}$	3.8
Hexane (impurity)				
Baker Resi	$6.54 \times 10^{-1*}$	1.06	4.57×10^{-1}	1.52

*Each tetraCDF is present of impurity in the other tetraCDF with the major isomer in each experiment designated by a superscript.

Table 2. Rate Constants and Half-Lives for the Photodecomposition of TetraCDF Isomers Exposed in Water to 300 nm Radiation or Sunlight (September).

Light Source/ Water Source	Rate Constants and Half-Lives			
	2,3,7,8-tetraCDF		1,2,7,8-tetraCDF	
	k (hr ⁻¹)	$t_{1/2}$ (hr)	k (hr ⁻¹)	$t_{1/2}$ (hr)
(A) Photoreactor				
HPLC Water	4.5×10^{-1}	1.54	3.0×10^{-1}	2.31
HPLC Water (Quartz cell)	7.02×10^{-1}	0.98	1.02	0.68
(B) Sunlight*				
HPLC Water	6.5×10^{-2}	10.7	8.19×10^{-2}	8.46
Distilled Water	6.2×10^{-2}	11.2	9.09×10^{-2}	7.63
Hudson River	1.18×10^{-1}	5.87	1.65×10^{-1}	4.20
Saratoga Lake	1.10×10^{-1}	6.30	1.47×10^{-1}	4.72