

Effect of Solvents on the Photodegradation Rates of Octachlorodibenzo-p-dioxin

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Commercially produced pentachlorophenol that is used primarily as a wood preservative may contain up to 2000 µg/g of OCDD¹ along with smaller amounts of less highly chlorinated dioxins and furans. In comparison to some CDD's, OCDD is much less toxic (Mamantov, 1984). The possibility that OCDD could be photolytically degraded to some of the more toxic CDD's has resulted in a number of publications that address that phenomenon.

Buser (1976) demonstrated that irradiation of solutions of OCDD or OCDF in hexane with γ -rays or UV light produced a number of different less highly chlorinated dioxins or furans. The major reaction pathway was reductive dechlorination resulting in CDD's or CDF's with 3 to 7 chlorines.

For the photolysis of OCDD in hexane with natural sunlight, Dobbs (1979) identified the major HpCDD and HxCDD intermediate products as the 1,2,3,4,6,7,9-HpCDD and 1,2,4,6,7,9-HxCDD isomers, respectively. These results indicated that the replacement of a Cl atom by H occurred most readily at one of the 2,3,7, or 8 numbered C positions and that formation of 2,3,7,8-TCDD did not easily occur under these conditions.

Studies of the formation of OCDD from PCP on the surface of treated wood indicated that the PCP carrier solvent could influence the levels of OCDD present (Lamparski *et al.*, 1980). For Dowicide EC7, when petroleum oil was used as the carrier, the

¹Abbreviations: octachlorodibenzo-p-dioxin, OCDD; octachlorodibenzo-furan, OCDF; chlorinated dibenzo-p-dioxin, CDD; chlorinated dibenzo-furan, CDF; heptachlorodibenzo-p-dioxin, HpCDD; hexachlorodibenzo-p-dioxin, HxCDD; tetrachlorodibenzo-p-dioxin, TCDD; pentachlorophenol, PCP.

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concentration of OCDD was only about 1% of the amount found in technical PCP (i.e., there was no formation of OCDD from PCP with this P9-A oil).

Generally, the more highly chlorinated CDD's are photolyzed more rapidly than the less highly chlorinated CDD's (Mamantov, 1984). A linear correlation between relative biological potency and photolysis half-lives was also noted for certain isomers of CDD's.

Choudhry and Webster (1985a, 1985b) determined the quantum yield for the photodegradation of CDD's using simulated artificial sunlight. These results also indicated that OCDD is less rapidly degraded than some of the other chlorinated CDD's. Desiderio et al. (1979) photolyzed 2,3,7,8-TCDD in isoctane, hexane, and cyclohexane and found little difference in the rates of degradation with the different solvents. Other studies with 2,3,7,8-TCDD examined the effects of solubilization (Botre et al., 1978), photochemical reduction (Crosby, 1978), and of different surfaces (Crosby and Wong, 1977). The primary objective of this study was to determine if the presence of different solvents affected the rate of photolysis of OCDD and also to determine the effect of these solvents on the photolysis products.

MATERIALS AND METHODS

Octachlorodibenzo-p-dioxin (OCDD) was purchased from Analabs (New Haven, Connecticut, USA). Benzene (B & J), hexane (B & J, UV), and acetonitrile (B & J, UV) were used as solvents in this study. 1,3-Cyclohexadiene, benzophenone, triethylamine, and cyclohexene were purchased from Aldrich Chemical Company. Potassium ferrioxalate was obtained from Alfa Products, Ventron Corporation. Water was obtained from a Corning megapure still equipped with a Barnstead deionizing column.

OCDD was dissolved in selected solvents by use of an ultrasonic water bath with the starting concentration of OCDD in the solvent mixtures in the range of 4.3×10^{-5} to 7.0×10^{-5} M (~ 28 μ g/ml). Two mls of OCDD solutions were placed in Pyrex glass tubes (1.0 cm i.d.) and irradiated for selected times (4 to 48 hours) in a carousel type apparatus (Moses, 1969). The light source was a 125 Watt medium-pressure mercury lamp contained in a quartz immersion well (Applied Photophysics). A solution of potassium chromate (0.27 g/l) and sodium carbonate (1.00 g/l) in water (Bass and Cerfontain, 1979) was circulated through the lamp jacket between the mercury lamp and the reaction solutions. This filter solution transmits light in the region of 295-350 nm (Choudry and Webster, 1985). The reaction solutions were removed from the photochemical reactor at selected times and the amount of unphotolyzed OCDD was determined. Five replicate samples were irradiated for each solvent mixture.

The amount of OCDD remaining in photolyzed samples was determined with a Tracor 560 GC/ECD equipped with a Hewlett-Packard 3390A integrator. The GC conditions were as follows: Pyrex glass column (1.8 m x 6.3 mm) packed with 3% SP-2250; initial temperature, 170°C; hold time, 10 minutes; program rate, 8°C/minute; final temperature, 300°C; final hold, 20 minutes; injection temperature, 300°C; ECD temperature, 350°C.

Mass spectral data were acquired with a Carlo Erba/Kratos MS80RFA GC/MS equipped with a J&W DB-5 capillary column (30 m x 0.25 mm i.d.). The operating conditions for the GC were as follows: Initial temperature, 100°C; hold time, 2 minutes; program rate, 8°C/minute; final temperature, 300°C; final hold, 20 minutes. The mass spectrometer was operated in the electron impact mode at 70 eV with a source temperature of 250°C.

The intensity of light was determined periodically throughout the experiments by using the potassium ferrioxalate actinometer (Hatchard and Parker, 1956; Calvert and Pitts, 1966). After 2 mls of potassium ferrioxalate solutions (0.006 M) were irradiated in Pyrex glass tubes for 2-5 minutes, the OCDD solutions were irradiated on the merry-go-round apparatus. The intensity of the incident light was calculated according to the method of Calvert and Pitts (1966).

RESULTS AND DISCUSSION

The preliminary experiments of photolysis of OCDD solutions indicated that irradiation time between 4 hours and 48 hours was the best reaction time for this study. Also, several experiments indicated that the presence or absence of oxygen had no measurable effect on the rate of disappearance of OCDD when irradiated in hexane or benzene.

Table 1. Molar absorptivity values of OCDD in selected solvents.

Solvent	Molar absorptivity (1 mole ⁻¹ cm ⁻¹)
Hexane	2251 (314 nm)
60% Acetonitrile/water	2339 (314 nm)

The molar absorptivities for OCDD in hexane and 60% acetonitrile/water are shown in Table 1. These UV absorption spectral data were used for the calculation of the quantum yields of OCDD in the respective solutions. The measured molar absorptivities of OCDD in the other solvents tested were somewhat widely varied. This variation was attributed to the low

concentration of OCDD and to the low molar absorptivity at this wavelength. Benzophenone has a molar absorptivity of $50 \text{ L mole}^{-1} \text{ cm}^{-1}$ at 313 nm and contributes to the absorption at this wavelength.

Measured light intensities for irradiation times of 2.0, 3.0, 4.0, and 5.0 minutes were 3.91×10^{-6} , 3.18×10^{-6} , 3.03×10^{-6} , and 3.65×10^{-6} einsteins $\cdot\text{l}^{-1}\cdot\text{s}^{-1}$, respectively. These measurements indicated the actinometer was not depleted by 5-minute exposures. The light intensity was calculated by using a quantum yield of 1.24 (Hatchard and Parker, 1956). In the case of 4 min. irradiations, the measured light intensity ranged from 3.03×10^{-6} to 3.44×10^{-6} einsteins $\cdot\text{l}^{-1}\cdot\text{s}^{-1}$ with an average of 3.13×10^{-6} (Table 2).

Table 2. Determination of intensity of light using KFeO_x actinometer.

Photochemical cell number	Light intensity (10^{-6} einsteins $\text{l}^{-1} \text{ s}^{-1}$)
I	3.10
II	3.22
III	3.03
IV	3.18
V	3.29
VI	3.03
VII	3.10
VIII	3.14
IX	3.07
X	3.10
<hr/> Irradiation time: 4 min.	
3.13 (0.08)*	

*Mean (standard deviation).

Regression analysis $\ln(c/c_0)$ vs t data were used to calculate the pseudo first order rate constants for all experiments. This relationship was essentially linear throughout the entire time of photolysis.

A comparison of the photolysis rates of OCDD in hexane and acetonitrile/water indicates the conversion of OCDD to products is about 30 times faster in hexane than in acetonitrile/water (Table 3). The photolysis rate was increased when 1,3-cyclohexadiene, triethylamine, or cyclohexene was used with OCDD in hexane. There are a number of effects that could cause this increase. If the molar absorptivity of OCDD increased due to the difference in solvent polarity, then the photolysis rate could increase. However, an increase in molar absorptivity was not observed in the UV absorption spectrum.

Table 3. Comparison of photodegradation rates, half-lives, and quantum yields of OCDD in selected solvents.

OCDD in selected solvents	First order rate constant (10^{-6} sec^{-1})	Half-life (hours)
5% 1,3-		
Cyclohexadiene/hexane	82.50 \pm 8.6	2.33
5% Triethylamine/hexane	72.77 \pm 6.3	2.65
5% Cyclohexene/hexane	40.50 \pm 1.7	4.81
Hexane	22.60 \pm 1.2	8.52
5% Benzene/hexane	13.40 \pm 0.46	14.4
5% Benzophenone/hexane	11.19 \pm 0.51	17.2
Benzene	6.03 \pm 0.20	31.9
60% Acetonitrile/water	0.75 \pm 0.27	257

^aMean \pm s.d.

^bAll the values are the mean of five replicate sample analyses.

All of the cosolvents utilized in these experiments, with the exception of benzophenone ($\epsilon_{313} = 50$), are transparent in the 295 to 340 nm spectral region (Murov, 1973). The lack of UV absorption by these cosolvent molecules precludes the possibility that photosensitization is a major factor in the photochemical process in these experiments. Likewise, the attenuation of incident light by cosolvents other than benzophenone should not contribute to a decrease in the rate of photolysis.

One explanation for the observed differences in photolysis rates is that some cosolvents are better H donors than hexane for the photolytically generated heptachlorodibenzo-p-dioxin radicals. The stability of the newly generated solvent radical would be a factor in determining the efficiency of H donor capability of each solvent. That the commonly accepted order of radical stability is allyl $>$ $3^0 > 2^0 > 1^0 >$ vinyl lends some support to this explanation.

The reaction quantum yield (Φ) of OCDD was calculated using the following equation (Choudhry and Webster, 1985a):

$$\Phi = \frac{K}{2.303 I_\lambda \epsilon_\lambda L}$$

where:

- K = photolysis first order rate constant for an individual OCDD solution (sec^{-1})
- I = the intensity of the incident light of wavelength (λ) (einsteins/l.sec)
- ϵ = the molar absorptivity ($1/\text{mol}\cdot\text{cm}$) at 313 nm
- L = the cell pathlength (cm)

The approximate quantum yields for the reaction of OCDD in hexane and 60% acetonitrile/water were 12.6×10^{-4} and 0.41×10^{-4} , respectively. The quantum yield (0.41×10^{-4}) for OCDD in 60% acetonitrile/water was in reasonably good agreement with the previously published value of 0.23×10^{-4} (Choudhry and Webster, 1985b). This small difference is possibly due to the difficulty in determining the molar absorptivity coefficient at that wavelength.

The major photoproducts of OCDD in selected solvents were identified by mass spectrometry. It was observed that for the photolysis of OCDD in hexane, 5% cyclohexene/hexane and 5% benzene/hexane, the predominant intermediate product was 1,2,3,4,6,7,9-HpCDD. By comparison of the retention time of 1,2,3,4,6,7,8-HpCDD standard with that of HpCDD, the first eluting HpCDD isomer was 1,2,3,4,6,7,9-HpCDD. As Buser (1976) suggested, the preferential loss of the chlorine atoms on the dibenzo-p-dioxin ring were the 2, 3, 7, and 8 positions. However, for the photolysis of OCDD in 5% 1,3-cyclohexadiene/hexane, preferential substitution of chlorine was on the 1,4,6, or 9 numbered carbons and the predominant intermediate seven chlorine isomer was 1,2,3,4,6,7,8-HpCDD.

In the GC/MS analysis of substituted products in benzene, one compound with a molecular ion of 154 and two compounds with a molecular ion of 498 were observed. On the basis of the mass spectrum, the identities of these compounds were established as biphenyl and two isomers of phenyl-HpCDD, respectively. With OCDD in cyclohexadiene/hexane, molecular ions of m/e 160 and 500 were observed. On the basis of the mass spectrum, the identities of these compounds were established as dimers of cyclohexadiene and cyclohexadiene-HpCDD, respectively. With OCDD in cyclohexene/hexane, the mass spectrum had a molecular ion peak at m/e 502. The identity of this compound was established as cyclohexene-HpCDD isomer, in which one chlorine atom had been replaced with a cyclohexene group. Also, the GC traces showed that these compounds had retention times longer than that of OCDD. Unidentified compounds with GC retention times longer than OCDD were observed with OCDD photolyzed in hexane (Dobbs, 1979).

Results from this study show that the rate of photolysis of OCDD in the 295 to 340 nm region is greatly affected by the surrounding solvent medium. The measured first order rate constants indicate that photolysis occurs more rapidly in solvents that are good H donors. The formation of 2,3,7,8-TCDD by photolysis of OCDD would not be expected to occur under these conditions.

In all solvent mixtures, except where 1,3-cyclohexadine was used, 1,2,3,4,6,7,9-HpCDD was the preferred isomer of that intermediate. This result is in agreement with previous publications. The identification of HpCDD-solvent substituted compounds had not been reported in the literature reviewed for

this publication, but the occurrence of these compounds is in agreement with the general mechanism suggested by Crosby (1978) for the photochemical reduction of aromatic halides.

REFERENCES

Baas P, Cerfontain H (1979) Photochemistry of γ -Oxo-oximes J Chem Soc Perkin Trans 2:151-155

Botre C, Memoli A, Alhaique F (1978) TCDD solubilization and photodecomposition in aqueous solutions. Environ Sci Technol 12:335-336

Buser HR (1976) Preparation of qualitative standard mixtures of polychlorinated dibenzo-p-dioxins and dibenzofurans by ultraviolet and gamma-irradiation of the octachloro compounds. J Chromatogr 129:303-307

Calvert JG, Pitts JN (1966) Photochemistry, New York, Wiley. 686-786

Choudhry GG, Webster GRB (1985) Kinetics and quantum yields of the photodegradation of 1,2,3,4,7-penta- and 1,2,3,4,7,8-hexachlorodibenzo-p-dioxin in aqueous acetonitrile. Chemosphere 14:9-26

Choudhry GG, Webster GRB (1985) Quantum yields of polychlorinated dibenzo-p-dioxins (PCDD's) in water-acetonitrile mixtures and their environmental phototransformation rates. Abstracts 189 National Meeting of the ACS, Miami, Florida, Paper No. G-37

Crosby DG, Wong AS, Plimmer JR, Woolson EA (1971) Photodecomposition of chlorinated dibenzo-p-dioxins. Science 73:748-749

Crosby DG, Wong AS (1977) Environmental degradation of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). Science 195:1337-1338

Crosby DG (1978) Conquering the monster--the photochemical destruction of chlorodioxins. ACS Symp Series 73:1-12

Desideri A, Domenico D, Vanzati R, Tancioni P, Muccio D (1979) Photolysis of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) in iso-octane, hexane and cyclohexane. Bull Chim Pharm 118:274-281

Dobbs AJ, Grant C (1979) Photolysis of highly chlorinated dibenzo-p-dioxins by sunlight. Nature 278:163-165

Hatchard CG, Parker CA (1956) A new sensitive chemical actinometer. II. Potassium ferrioxalate as a standard chemical actinometer. Proc Roy Soc A235: 518

Lamparski LL, Stehl RH, Johnson RL (1980) Photolysis of pentachlorophenol-treated wood. Chlorinated dibenzo-p-dioxin formation. Environ Sci Technol 14:196-200

Mamantov A (1984) Linear correlation between photolysis rates and toxicity of polychlorinated dibenzo-p-dioxins. Environ Sci Technol 18:808-810

Moses FG, Liu RS, Monroe BM (1969) The "Merry-Go-Round" Quantum Yield apparatus. Mol Photo Chem 1:245-249

Murov SL (1973) Handbook of photochemistry, New York, Marcel Dekker, Inc. 3

Wayne RP (1970) Photochemistry, London, Butterworths. 183-184

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