

## APPENDIX

Pentachlorophenol (PCP), a fungicide, has been widely used for the preservation of lumber, and in 1985, its production peaked at about  $10^8$  kg/yr (34). This widespread use has led to high levels of PCP contamination in a variety of matrices including rain (34, 37-39). In 1976, it was found that high concentrations of aqueous PCP under basic conditions can be converted to octachlorodibenzo-*p*-dioxin (OCDD) (40). Further research showed that when aqueous PCP at a concentration as low as 1 mg/L is irradiated at wavelengths of less than 290 nm, OCDD and lesser amounts of heptachlorodibenzo-*p*-dioxin (HpCDD) are generated (41, 42). We have investigated this reaction further, and we have confirmed that this reaction occurs when environmentally significant wavelengths greater than 290 nm are used even at PCP levels as low as 100 ppb and at a realistic rain pH of 5.5.

**Experimental.** 99% pure  $^{13}\text{C}_6$  PCP was purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA) and diluted with acetone to a concentration of 1.2  $\mu\text{g/mL}$ . The PCP solution was spiked into a 1-L quartz Erlenmeyer flask (Ace Glass, Louisville, KY) and diluted with HPLC grade water to give a PCP concentration of between 100 and 1000  $\mu\text{g/L}$ . This allowed us to investigate this reaction at concentrations as much as an order of magnitude below the lowest concentrations previously studied. The flasks were placed 30 cm from a medium pressure mercury lamp (Ace Glass, Louisville, KY) and stirred. The lamp was enclosed by a water-cooled glass sleeve which eliminated wavelengths below 290 nm. These solutions were not buffered; however, the initial pH for each flask was about 5.5, similar to the pH of rain. The solutions were then irradiated for a period of between 45 min and 4 hours. The light power was monitored using a PMA 2100 pyranometer (Solar Light Co., Philadelphia, PA) and integrated over the reaction time. When the reaction time was completed, a solution of unlabeled PCDD/F

with congeners representing each homologue group was spiked onto the solution as the internal standard. Dark experiments were also performed alongside the above reaction vessels; for these experiments, the flask was wrapped in aluminum foil to prevent light from entering the solution. All solvents were purchased from EM Science, Gibbstown, NJ.

Upon completion of the reaction, 50 mL of hexane was added to the flask. About 50 g NaCl was also added to the flask to facilitate the extraction of PCDD/F from the water layer. This solution was transferred to a separatory funnel and shaken. The flask was then rinsed with 50 mL of hexane that was then transferred to the separatory funnel. After two layers had formed, the hexane fraction was placed in a round bottom flask, and the water was extracted two more times with 50 mL hexane. The extracts were combined, and the residual water in the hexane fraction was removed using anhydrous sodium sulfate. The hexane fraction was then reduced to a volume of about 1 mL by rotary evaporation and placed in an 8 mL amber vial, where its volume was further reduced by nitrogen blow-down to 100  $\mu$ L.

PCDD/F were quantitated using the internal standard approach, and analysis was performed on a Hewlett Packard 5973 gas chromatographic mass spectrometer operating in the electron capture, negative ionization mode. Chromatographic separation was achieved using a 30 m, DB-5MS, capillary column (250  $\mu$ m i.d.; 0.25  $\mu$ m film thickness; J&W Scientific, Folsom, CA). Helium was used as the carrier gas. The sample (2  $\mu$ L) was injected with a 25 psi pulsed injection in the splitless mode. Temperature programming was as follows: isothermal for 2 min at 110  $^{\circ}$ C, 30  $^{\circ}$ C/min to 210  $^{\circ}$ C, 2  $^{\circ}$ C/min to 280  $^{\circ}$ C, isothermal for 10 min. The flow of the reagent gas, methane, in the mass spectrometer's ion source was maintained at 40% of the total flow or at 2  $\text{cm}^3/\text{min}$ , which gave a manifold pressure of  $2 \times 10^{-4}$  Torr. The ion source temperature was held at 150  $^{\circ}$ C. Two ions from each homologue group were monitored using selected ion moni-

toring to enhance sensitivity, and a peak was only classified as a PCDD/F if its mass spectral intensities were in the correct, predicted isotopic ratio (4).

**Results and Discussion.** We first analyzed the  $^{13}\text{C}_6$  PCP spiking solution by GC/MS to make sure that any PCDD/F detected was not a contaminant in the original standard. The mass chromatograms showed that the standard was clear of any PCDD/F. As a second quality control measure, dark experiments were conducted so that we could rule out any pathway of PCDD/F production other than a photochemical reaction. No PCDD/F were detected in any dark experiments.

Table A-1 gives the mass of PCDD/F produced in the five different experiments. In order to investigate the effect of the hydroxyl radical (OH) on this reaction, two of these experiments included hydrogen peroxide at a concentration of 100 ppb. The best conversion rate is seen in the experiment containing hydrogen peroxide and 1 mg/L PCP. Irradiation of this experiment lasted for 4 hours, giving a yield of 0.1% by mass for the conversion of PCP to OCDD. This experiment also showed the formation of HpCDD with a yield of about 0.01 % and HxCDD with a yield of about 0.003%. The two experiments that had the lowest concentration of PCP still showed conversion to OCDD, but at a lower yield. Since the experiment that had 100  $\mu\text{g}$  PCP and 100 ppb  $\text{H}_2\text{O}_2$  had a lower yield compared to the experiment with 1 mg PCP and 100 ppb  $\text{H}_2\text{O}_2$ , it seems likely that the proportion of  $\text{H}_2\text{O}_2$  to the reactant is important. This ratio is high in the first experiment, so the PCP may be degrading by a different pathway. It is also important to note that the experiments in which no  $\text{H}_2\text{O}_2$  was added still showed a conversion of PCP to OCDD. These experiments were irradiated for 45 min and showed yields of between 0.006% and 0.0007%.

The purpose of this experiment was to confirm that PCDD/F is generated from PCP photochemically at environmentally relevant pH levels and to show that wavelengths less than 290 nm are not necessary to initiate this reaction. This is important because sunlight with wavelengths less than 290 nm do not reach the troposphere and because previous work had used pH levels of 7.0 or higher (40, 42). Our data suggest that available sunlight in the troposphere may convert environmental levels of PCP in the atmosphere, particularly in the condensed aqueous phase, to PCDD/F.

**Table A-1:** Conversion of  $^{13}\text{C}_6$  PCP to  $^{13}\text{C}_{12}$  PCDD under Varying Irradiation Conditions.

Mass PCP*	Vol. $\text{H}_2\text{O}_2$	Time Irradiated (Total Energy)	$^{13}\text{C}_{12}$ HxCDD formed (ng)	$^{13}\text{C}_{12}$ HpCDD formed (ng)	$^{13}\text{C}_{12}$ OCDD formed (ng)
100 $\mu\text{g}$	100 $\mu\text{L}$	4 hr (70 $\text{J}/\text{cm}^2$ )	0	0	0.5
1000 $\mu\text{g}$	100 $\mu\text{L}$	4 hr (70 $\text{J}/\text{cm}^2$ )	30	140	1,100
100 $\mu\text{g}$	0	45 min (10 $\text{J}/\text{cm}^2$ )	0	0.8	6
1000 $\mu\text{g}$	0	45 min (20 $\text{J}/\text{cm}^2$ )	0	0	7
1000 $\mu\text{g}$	0	45 min (20 $\text{J}/\text{cm}^2$ )	0	0	2

\* in 1 liter of water