FORMATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS DURING PHOTOLYSIS OF PENTACHLOROPHENOL IN AQUEOUS SOLUTION

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Introduction

The photolytic condensation of chlorophenols has been widely studied. The phototransformations of thin layers of pentachlorophenol (PCP) has shown the products of heptachlorodibenzo-p-dioxin (H_7CDD) and octachlorodibenzo-p-dioxin (OCDD)[1]. Irradiation of alkaline aqueous solution of PCP has been reported to produce OCDD[2]. It also has been proved that the irradiation of several PCP-containing aqueous solutions indicated the formation of higher chlorinated PCDD/Fs[3]. Laboratory studies have been conducted to determine the effect of sunlight on the concentrations of PCP and PCDDs in wood treated with PCP[4]. The present studies were undertaken to investigate the factors that affected the formation of PCDD/Fs during photolysis of PCP in aqueous solutions.

Materials and Methods

All solvents used were of analytical grade. Triple distilled water (from $KMnO_4$ and $K_2Cr_2O_7$) was used. PCP, whose purity has been described by the manufacturer as 99%, was purified as described to remove impurities of PCDD/Fs[3]. ^{13}C-labelled 2,3,7,8-substituted PCDD/Fs congeners were obtained from Cambridge Isotope Laboratories. Photolysis experiments were conducted by exposing aqueous solutions of PCP to light emitted by a 300 w medium-pressure Hg-lamp. A Agilent 6890 GC/5973N MS equipped with a HP-5 MS (60 m ×0.32 mm, Agilent). was used for analyses of the photoproducts.

Some chemicals were added to the solution of PCP whenever it was necessary. The solutions (350 ml) were filled in the cylindrical glass tube. During the irradiation, the solutions were stirred and the temperature of the solutions was about 20 °C.

Results and Discussion

The irradiation of the solution of PCP indicated the formation of higher chlorinated PCDDs and PCDFs. Contents of 2,3,7,8-congeners of PCDD/Fs formed from photolysis of PCP under the applied conditions are shown in Table 1. The main products of PCDD/Fs were OCDD and OCDF. Tetra- to heptachlorinated dibenzo-p-dioxins and dibenzofurans could be produced by condensation of PCP or photoinduced dechlorination of OCDD/F. The pattern of PCDD/Fs congeners in this study was agree with that determined by Vollmuth et al.[3].

One important result of free radical formation in the photochemical transformation of PCP is the production of PCDD/Fs. The increasing rate of photodecomposition of PCP with increasing pH, provided the evidence that ionic mechanism was not in favor of free radical reactions and thus decreasing the amount of PCDD/Fs.

Iodine free radical can be easily produced after irradiation of iodine solution. A iodine free radical could attack a molecule of PCP to form perchlorinated free radical and their hydroperoxide derivatives. Recombination of corresponding phenyl-type radical resulted in the formation of hepta- and octa-isomers of PCDD/Fs (Figure 1).

FORMATION AND SOURCES

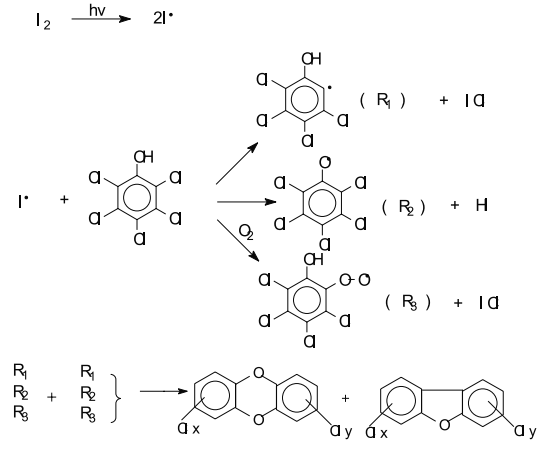

Figure 1. Supposed mechanism of free radical pathway to formation of PCDD/Fs

Table 1. Contents of 2,3,7,8-congeners of PCDD/Fs formed from the photolysis of 22 mg/l PCP solution in irradiation of 40 minutes (ng/mg PCP)

PCDD/Fs	Water (pH:5.61)	pH:6.21	Iodine: 22 mg/l
2,3,7,8-TCDD	ND	ND	0.57
2,3,4,7,8-PCDF	ND	ND	0.89
1,2,3,7,8-PCDD	3.70	6.53	6.57
1,2,3,4,7,8-H_6CDF	ND	0.46	1.41
1,2,3,4,7,8-H_6CDD	2.06	2.75	6.26
1,2,3,6,7,8- H_6CDD	1.19	4.77	10.86
1,2,3,7,8,9- H_6CDD	4.29	4.39	12.02
1,2,3,4,6,7,8-H_7CDF	2.48	8.55	19.22
1,2,3,4,7,8,9-H_7CDF	ND	0.75	2.48
1,2,3,4,6,7,8- H_7CDD	4.62	23.65	38.31
OCDF	3.26	13.38	22.68
OCDD	10.58	43.36	73.51
Total 2,3,7,8-substituted PCDD/Fs	32.18	108.59	194.78

ND: <0.01 ng/mg PCP

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