

Ultraviolet Degradation of Polychlorinated dibenzo-p-dioxins and Dibenzofurans in Flue Gas from Pentachlorophenol Combustion

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Introduction

The fate and diffusion of Polychlorinated dibenzo-p-dioxins and Dibenzofurans(PCDD/Fs) in the environment may involve volatilization, atmospheric transport, oxidation, reduction, bioaccumulation, bio- and photodegradation, etc. Photodegradation is probably the most important mechanism of PCDD/Fs removal from the environment¹. As a result, a number of studies on this subject have been reported in the literature². The majority of these studies have been devoted to the photolysis of standard PCDD/Fs solution in different organic solvents such as methanol, hexane, toluene, carbon tetrachloride etc. Dechlorination is generally reported as the predominant reaction. Only a few studies claim that photodechlorination is not the most significant pathway of PCDD/Fs decomposition and suggest that C-O bond cleavage may be an important photolysis route¹.

However, there is little literature about photolysis of PCDD/Fs in flue gas. The aim of this study was to investigate the photolysis characteristic of PCDD/Fs in flue gas from pentachlorophenol (PCP) combustion at different temperature in a tube furnace in order to get more information on both the photodegradation rate and pathway.

Materials and methods

Experiments were conducted in an electrically heated, quartz tube flow reactor, at temperature ranging from 400°C to 700°C with 100°C increments. Figure 1 and 2 shows the experimental apparatus. There were two quartz tubes in the same combustion condition. High purity PCP reactant (15mg) was placed in a sampling boat. Air carrier gas was supplied at 200ml/min of flow rate into the quartz tube. Reactor residence time of all the experiments was 30min. The PCDD/Fs in flue gas produced from PCP combustion were collected by a dual ice-cooled toluene trap. One quartz tube was connected to the photolysis system, and the other was directly connected to the toluene trap. The light source is a low pressure mercury lamp emitting light at 254nm and the irradiation intensity was 12mw/cm².

After each experiment, PCDD/Fs in the toluene solution and rinses were combined, then concentrated, cleaned up. The detailed pretreatment procedures are described elsewhere according to USEPA method 8280B^{3, 4}. All analyses were carried out on a high resolution gas chromatograph (HRGC) coupled to low resolution mass spectrometer (LRMS). 1 µl volumes of the samples were injected by splitless mode. Separation was performed on a DB-5 capillary column (60 m length, 0.25 mm I.D., 0.25 µm film thickness). Helium was used as the carrier gas and flow was 1.2 ml/min at constant flow mode. The temperature program for GC oven was: initial temperature 100°C, held for 2 minutes; 100~200 °C at 25°C/minute; 200~280°C at 5°C/minute; 280°C held for 30 minutes. Mass spectrum condition: electron impact ionization 70 eV; electron multiplier voltage 420V; ion source temperature 220°C; inlet temperature 250°C; SIM (selected ion monitoring mode).

Results and Discussion

The photodegradation rate of total PCDD/Fs concentrations and I-TEQs are shown in Figure 3. It appeared that the total concentrations of PCDD/Fs photodegraded in all the examined temperature with photodegradation rate ranges from 10.8% to 99.7%. The highest photodegradation rate carried out at 400C. However in the experiments at 500°C and 700°C, the I-TEQs increased after irradiation, primarily due to the dechlorination of OCDD. Although the toxicity of OCDD is the lowest of the seventeen 2,3,7,8 -substituted congeners, the potential exists for conversion of OCDD to the lower chlorinated PCDDs, which may result in greater toxicity⁴.

It can be seen from Figure 4 that the PCDD/Fs products of PCP combustion were only PCDDs at 400°C and 500°C. When the alkali salts of chlorinated phenols are heated, PCDDs are formed at temperature above 250 °C. Weber found dibenzofurans were formed at temperature above 350 °C⁵. In our experiments, PCDFs formed at 600 °C when PCP was combusted. This may be due to different experiment condition. In Weber's experiments, chlorophenol was sealed in quartz ampoules. The photodegradation products of PCDD/Fs were the same homologues, i.e., only PCDDs after irradiation, which mean C-O bond of PCDDs could not cleave, resulting in formation of PCDFs. OCDF occurred with small amounts when temperature increased to 600 °C and the ratio of PCDF/PCDDs increased distinctly after irradiation, which due to the formation of lower chlorinated PCDFs.

Comparison the homologue profile of PCDD/Fs produced from PCP combustion at 500 °C and 600°C revealed the different photodegradation pathway (see Figure 5 and 6). Dechlorination was the predominant reaction when PCP combusted at 500 °C. The photolysis products of PCDD/Fs were HxCDD and HpCDD, i.e., higher chlorinated PCDDs. The formation of TCDD, HpCDD, OCDD and OCDF was observed when PCP combusted at 600 °C and OCDD was also the predominant product, whose concentration corresponds 96% of the total concentration of PCDD/Fs. Besides PCDDs, the PCDFs, PeCDF and HxCDF also formed after irradiation. This may be due to the formation of OCDF through the cleavage of C-O bond of OCDD, then dechlorinate to form lower chlorinated PCDFs. So there were two different photodegradation pathways for PCDD/Fs, which formed from PCP combustion at 600°C, irradiation by UV.

Acknowledgements

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Figure 1: Diagram of experimental apparatus

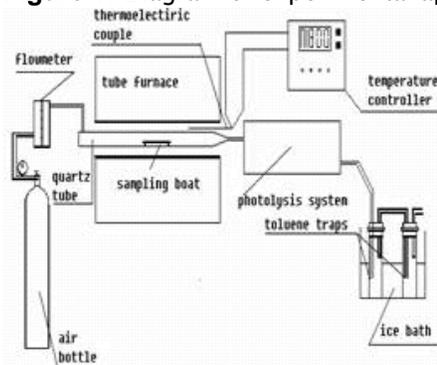


Figure 3: The photodegradation rate of PCDD/Fs

Figure 2: Diagram of photolysis system

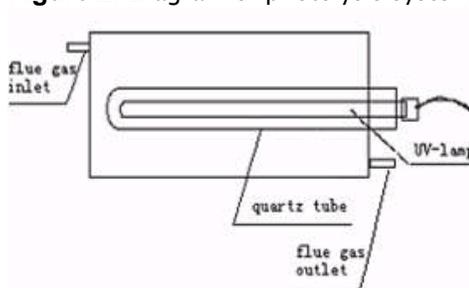


Figure 4: The ratio of PCDF/PCDD before and after irradiation

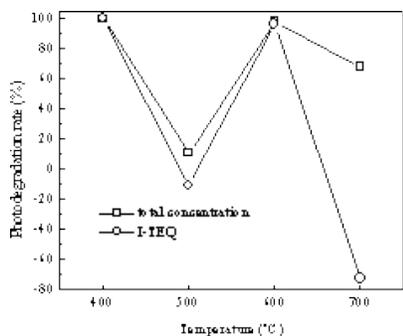


Figure 5: Homologue profiles of PCDD/Fs 500°C

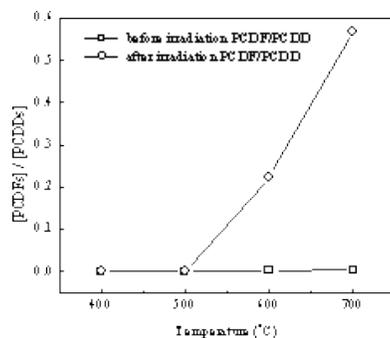
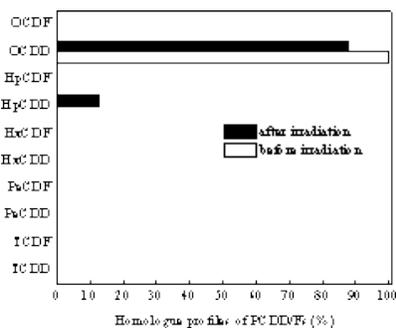


Figure 6: Homologue profiles of PCDD/Fs 600°C

