

DIOXIN FORMATION FROM TETRACHLOROPHENOL OVER FLY ASH UNDER BREAKTHROUGH CONDITIONS

Elmar Altwicker and Michael S. Milligan

The Isermann Department of Chemical Engineering
Rensselaer Polytechnic Institute
Troy, NY 12180-3590

Introduction

Laboratory studies of PCDD/F formation over municipal solid waste incinerator (MSWI) fly ash have shown a temperature peak for formation centered around 300°C. This appears to be true for the so-called *de Novo* synthesis reactions (1,2) as well as for reactions using specific gas phase precursors, i.e., chlorophenols (3). In addition, most of the measured PCDD/F products and unreacted chlorophenol precursors have been found adsorbed to the fly ash, in contrast to some actual incinerator data which suggest that much of the PCDD/F are in the gas phase. In this work we report on continuing studies of the formation rates of PCDD from gas phase chlorophenol precursors.

Experimental

2,3,4,6-Tetrachlorophenol (2,3,4,6-T₄CP) was reacted over actual MSWI fly ash in a laboratory fixed-bed reactor under both non-breakthrough (no precursor detected in the downstream trap) and breakthrough (precursor detected in the downstream trap) conditions. In the middle of a temperature-controlled 1.2 cm diameter and 45 cm long tubular reactor is a glass frit holding 0.1-1.0 gram samples of MSWI fly ash in place. Mixtures of oxygen and nitrogen are flowed using Tylan mass flow controllers at flow rates ranging from 20-100 ml/min at reaction temperatures from 250-400°C.

FORM

Chlorophenol precursors are added to the reactant stream by passing oxygen/nitrogen mixtures over a perpendicularly mounted stainless steel reservoir containing about 10 mg of precursor. By carefully controlling the precursor reservoir temperature, a constant flux of precursor to the gas stream is attained, resulting in a constant gas-phase concentration of precursor. In these experiments, gas-phase precursor concentrations ranged from 150-700 ng/ml. Before an experiment, the reactor is brought to the reaction temperature under a helium flow. Oxygen/nitrogen/chlorophenol mixtures are then flowed, while the outlet stream from the reactor is bubbled through a hexane impinger trap. After the desired reaction time, the reactor is quickly cooled with a helium stream. The outlet impinger sample and fly ash extract are separately analyzed by GC/MS for chlorophenols and PCDD/F (4).

Results

Figure 1 shows PCDD formation rates in $\mu\text{g/g-min}$ from 2,3,4,6- T_4CP as a function of temperature for two different quantities of fly ash charged to the fixed-bed reactor: 1.0 and 0.10 grams. In the latter case, the fly ash was diluted with 0.90 g of glass beads previously determined to be inactive to PCDD formation reactions. The precursor concentration was maintained at 350-400 ng/ml for reaction times ranging from 2-15 minutes. Prior experiments have shown that PCDD formation rates were constant with time under these conditions. For the case of 1.0 g of fly ash, all of the PCDD product was found adsorbed to the fly ash and no precursor was found in the downstream trap. The yield of PCDD peaked at 325°C with a maximum formation rate of 1.6 $\mu\text{g/g-min}$. However, when only 0.10 g of fly ash were charged to the reactor and identical experiments run, the results were markedly different. In these cases, unreacted 2,3,4,6- T_4CP was recovered in the downstream trap along with the majority of the PCDD product. Under these precursor breakthrough conditions, the rate of formation of PCDD increased with temperature to about 10 $\mu\text{g/g-min}$ before leveling at 400°C.

Identical experiments were run under these breakthrough conditions (0.10 g of fly ash) for two more gas-phase precursor concentrations: 150 and 700 ng/ml of 2,3,4,6- T_4CP . Figure 2 compares these results with those shown in figure 1 for 0.10 g of fly ash. At a precursor concentration of 150 ng/ml,

a PCDD formation peak was noticed at 350°C. When 700 ng/ml of precursor was flowed through 0.10 g of fly ash, the PCDD yield increased with temperatures up to 400°C. In all cases a significant fraction of unreacted precursor was found in the downstream trap, along with almost all of the PCDD product (a small fraction was found adsorbed to the fly ash). H₆CDD was the major product in all of these reactions, although H₇CDD and O₈CDD was detected in slightly increasing amounts as temperature increased. The amounts of H₆CDD and lower congeners were about two orders of magnitude less, and PCDF (mostly H₆CDF) were about 2-3 orders of magnitude less.

These experimental results can be interpreted in terms of a simple adsorption-reaction-desorption sequence. Because the PCDD product desorbs into the gas phase, decomposition and dechlorination reactions on fly ash cannot occur, particularly at the higher precursor concentrations where the PCDD seemed to be preferentially displaced by the incoming chlorophenol molecules. The precursor/fly ash ratio (i.e., the number of gas-phase precursor molecules available per adsorption/reaction site) clearly plays an important role in controlling PCDD-yields and formation rates.

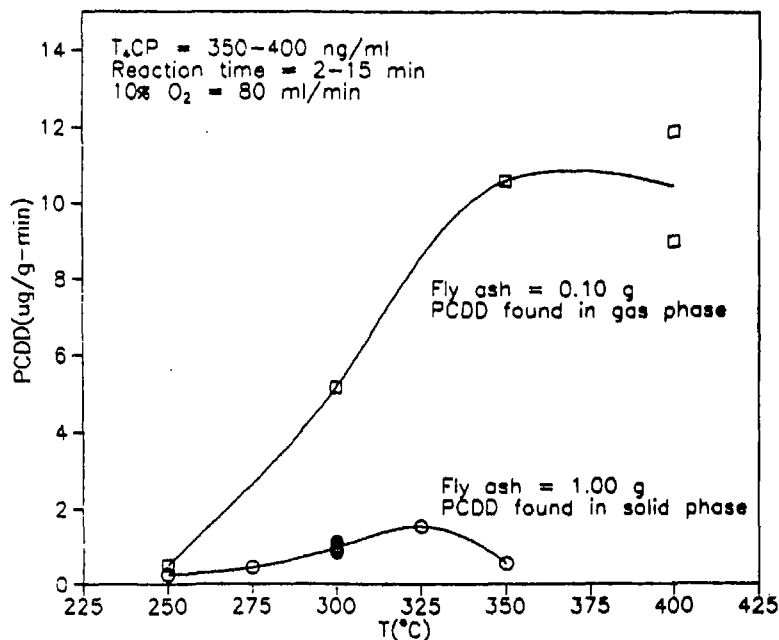


Figure 1. PCDD yields from the gas-phase precursor 2,3,4,6-tetrachlorophenol under breakthrough (0.10 g of fly ash) and non-breakthrough (1.0 g of fly ash) conditions.

FORM

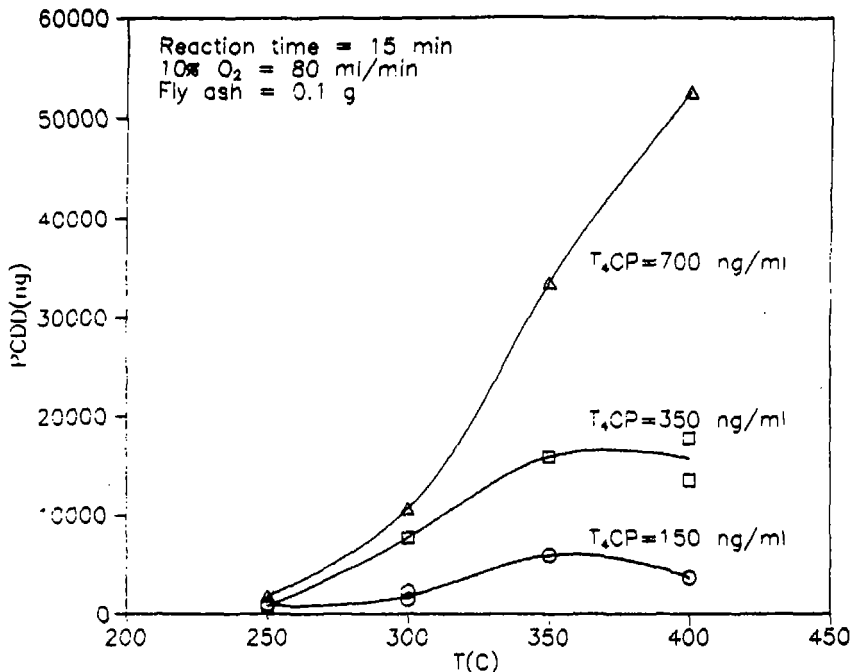


Figure 2. PCDD yields from the gas-phase precursor 2,3,4,6-tetrachlorophenol under breakthrough conditions for three gas-phase concentrations.

References

- (1) Milligan, M.S.; Altwicker, E. The Relationship between *de Novo* Synthesis of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans and Low-Temperature Carbon Gasification in Fly Ash. *Environ. Sci. Technol.*, in press.
- (2) Stieglitz, L.; Vogg, H. On Formation Conditions of PCDD/F in Fly Ash from Municipal Waste Incinerators. *Chemosphere* 1987, 16, 1917-1922.
- (3) Dickson, L.C.; Karasek, F.W. Mechanism of formation of Polychlorinated Dibenzo-p-dioxins Produced on Municipal Incinerator Fly Ash from Reactions of Chlorinated Phenols. *J. Chromatogr.* 1987, 389, 127-137.
- (4) Altwicker, E.R.; Milligan, M.S. Formation of Dioxins: Competing Rates between Chemically Similar Precursors and *de Novo* Reactions. *Chemosphere*, in press.